جامعة أم القرى

كلية العلوم التطبيقية

قسم الكيمياء

التفاعلات الكيميائية الصلبة لبعض المتراكبات الفلزية مع يوديد البوتاسيوم

رسالة مقدمة من

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ما جستير في العلوم (كيمياء)

وذلك كجزء من متطلبات الحصول على درجة الدكتوراه

في العلوم (كيمياء غير عضوية)

الإشراف

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مكة المكرمة

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IN THE NAME OF ALLAH
THE MOST GRACIOUS
THE MOST MERCIFUL

الله

بسم الله الرحمن الرحيم

الملخص العربي

تشمل الرسالة على ثلاثة فصول رئيسية:

الفصل الأول "المقدمة" ولتي تشتمل على جزئين رئيسيين للسرد المرجعي لكل من كيمياء الاحتكاك وكذلك لتفاعلات الاحتكاك للهيدرازيدات وبعض متراكبات الأثيرات التاجية.

الجزء الأول "تفاعلات كيمياء الاحتكاك" ويشتمل على تعريف لكيمياء الاحتكاك والاختلافات بين كيمياء الاحتكاك والكيمياء الميكانيكية وأخيراً فإن هذا الجزء يشتمل على السرد المرجعي لبعض تفاعلات كيمياء الاحتكاك المنشورة حديثاً في مجالات الكيمياء العضوية، كيمياء العضو فلزية والتفاعلات غير العضوية والكيمياء التناسقية.

وتعرف كيمياء الاحتكاك على أنها فرع الكيمياء الذي يتعامل ويدرس التغيرات الكيميائية والفيزوكيميائية للمركبات الصلبة نتيجة لتأثير الطاقة الميكانيكية.

ومن جهة أخرى يمكن تعريف الكيمياء الميكانيكية على انه فرع الكيمياء الذي يدرس ويتعامل مع التغيرات الكيميائية والفيزوكيميائية للمواد في مجالات التجمع المختلفة تحت تأثير الطاقة الميكانيكية. وترجع أهمية تفاعلات كيمياء الاحتكاك نظراً لتطبيقاته العديدة في الصناعات التكنولوجية والكيميائية والتعدينية والبناء.

ويشتمل الجزء الثاني على السرد المرجعي للهيدرازيدات وبعض متراكبات الأثيرات التاجية ويتضمن هذا الجزء أيضاً على السرد المرجعي للأبحاث المنشورة الحديثة لنا، كما أنها تشتمل على تحضير بعض المتراكبات الجديدة للنحاس الأحادي، النحاس الثنائي، الكوبلت الثنائي والكوبلت الثلاثي والمشتقة من الجيرارد T والفورمايل هيدرازين. ويشتمل هذا الجزء أيضاً على تحضير بعض متراكبات الزئبق الثنائي الجديدة والمشتقة من الأثيرات التاجية (DC 18 C 6 , DB 18 C 6) وينتهي هذا الفصل بالهدف من العمل.

يشتمل الفصل الثاني "الجزء العملي" على التفاصيل العملية المستخدمة في هذه الرسالة. وقد استخدمت في هذه الرسالة ثمانية مرتبطات والتي استخدمت في تحضير متراكبات النحاس الثنائي والأحادي والكوبلت الثنائي والثلاثي. وتشتمل هذه المرتبطات على (1- (كربكوسي ميثيل) بيردنيوم كلوريد الهيدرازين (G.P) ، ن - (3- هيدروكسي بيردين - 2 -يل) - N' - فينيل ثيويوريا ، - N - 2 (6 - مثيل بيرديل) N'- ثيويوريا، N { [(اليل أمينو) ثيوكسو مثيل] هيدرازينو كربونيل مثيل} ثلاثي ميثيل أمونيوم كلوريد ، N- { [(ايثيل أمينو) ثيوكسو ميثيل} هيدرازينو كربونيل ميثيل} ثلاثي ميثيل أمونيوم كلوريد و N { [(فينيل أمينو) ثيوكسو ميثيل] هيدرازينو كربونيل ميثيل } بيردنيوم كلوريد.

وقد حضرت متراكبات كلوريد الكوبلت والنحاس الثنائي باستخدام الطريقة الكيميائية المعتادة وذلك بتفاعل المرتبطات السابق ذكرها مع كلوريد النحاس ثنائي الماء وكلوريد الكوبلت سداسي الماء في الأيثانول. ومتراكبات النحاس الثنائي والأحادي والكوبلت الثنائي والثلاثي المقابلة حضرت باستخدام تفاعلات كيمياء الاحتكاك وذلك بتفاعل متراكبات الكلوريدات السابقة (المحضرة بالطريقة الكيميائية المعتادة) مع يوديد البوتاسيم في هون من الأجيت. وقد وصفت طرق تحاليل المتراكبات الصلبة وطرق تحضير المحاليل. وأخيراً يحتوي هذا الفصل على مناقشة الطرق المستخدمة والأجهزة (التوصيل الكهربائي، الأشعة تحت الحمراء، الأشعة المرئية وفوق البنفسجية وطيف الرنين النووي المغناطيسي للبروتون والقياسات المغناطيسية).

ويحتوي الفصل الثالث "النتائج والمناقشة" على النتائج التي حصل عليها والتراكيب المفروضة للمتراكبات الصلبة المفصولة. وقد وضحت نتائج التحليل العنصري (الكربون، الهيدروجين، النيتروجين، الكبريت والفلز) للمتراكبات الصلبة المفصولة بتطابق القيم النظرية مع المعملية. وقد اشتمل هذا الفصل على المواضيع التالية.

I. وصف تفصيلي لطرق تحضير المتراكبات الصلبة باستخدام طرق الكيمياء العادية وكذلك طريقة كيمياء الاحتكاك كما أنها تضمنت تقسيم المتراكبات طبقاً إلى الذرات المعطية والمتضمنة في الروابط، وقد افترضت الصيغ الكيميائية وتراكيب المتراكبات على أساس التحليل العنصري، نتائج التحليل الطيفي، والمغناطيسي. وقد أظهرت التحاليل الكيميائية للمرتبطات والمتراكبات المحضرة بالطرق الكيميائية العادية وطريقة الاحتكاك في الجداول 4، 5، 6.

II. مناقشة نتائج طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي للمرتبطات الثمانية وذلك للتحقق من تراكيبها وتعيين أهم مواضيع المجموعات الوظيفية وتعيين مواضع الارتباط.

III. مناقشة المتراكبات الصلبة والمشتقة من الطرق الكيميائية العادية كما يشتمل هذا الجزء على تعيين التراكيب الفراغية لكل من متراكبات النحاس الثنائي والكوبلت الثنائي باستخدام قياسات التوصيل الكهربائي، طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيس والقياسات المغناطيسية.

IV. مناقشة المتراكبات الصلبة والمشتقة من تفاعلات الاحتكاك، كما يوضح هذا الجزء التراكيب الفراغية لمتراكبات النحاس الأحادي والثنائي والكوبلت الثنائي والثلاثي باستخدام قياس التوصيل الكهربائي (طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي) والقياسات المغناطيسية.

وقد اقترحت جميع النتائج السابقة بأن هذه المرتبطات ترتبط إما في صيغة الكيتو أو الأينول ولكن معظمها فصل في صورة الكيتو، كما وضحت أيضاً النتائج بأن تفاعلات الاحتكاك تكون مصحوبة بعملية إحلال أيونات الكلوريد باليوديد. كما أن عملية تحضير المتراكبات بطريقة الاحتكاك تكون مصحوبة في بعض الحالات بأكسدة الكوبلت الثنائي إلى الثلاثي ولكن تتم عملية اختزال معظم

متراكبات النحاس الثنائي إلى النحاس الأحادي. و أخيراً وضحت النتائج التراكيب الفراغية لمعظم متراكبات النحاس الثنائي وأن معظمها لها شكل المجسم الثماني المشوه والقليل لها شكل الهرم الرباعي.

ومن الجهة الأخرى فإن متراكبات النحاس الأحادي لها شكل المربع المستوى. كما اقترحت النتائج بان الكوبلت الثنائي له شكل المجسم الثماني ذات المغزلية المرتفعة وقليل من هذه المتراكبات له شكل الهرم الرباعي. وأخيراً أوضحت النتائج بأن متراكبات الكوبلت الثلاثي لها شكل المجسم الثماني ذات المغزلية المنخفضة.

وتحتوي الرسالة على ستين مرجعاً علمياً، وقد وضحت الأشكال في ثمانين شكلاً وكذلك المتراكبات في أربعين تركيباً كيميائياً.

Umm Al-Qura University
Faculty of Applied Sciences
Department of Chemistry

TRIBOCHEMICAL REACTIONS OF SOME METAL COMPLEXES WITH POTASSIUM IODIDE

BY

SAWSAN M. A. AL-ASHQAR

(M. Sc. In Chemistry)

A THESIS

Submitted in Partial Fulfillment of the Requirements for the Degree of Ph.D. in Chemistry

(Inorganic Chemistry)

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DEDICATION

To:

My Father,

My Mother,

and

Brothers.

ACKNOWLEDGEMENT

First of all I do thank **Allah** for his bless to me and I pray for the best creation and messenger our Prophet Mohammed, Peace Be Upon Him.

I wish to express my thanks and gratitude to my supervisors, **Professor Mohammed M. Al-Qurashi and Professor Mohsen M. Mostafa**, for their suggesting the program of this research, supervision, support, guidance, encouragement, patience and valuable advice during the course of study.

Acknowledgement and thanks are also extended to all the staff members and colleagues in the Chemistry Department, Girls Section, for their help and moral support.

I thank **Professor Ahdualhadi M. Al-Umari, Head of Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University**, for providing the facilities for this research and the technical staff for their excellent services.

A lot of thanks are also due to the **Chairman of the Department of Chemistry, Professor Abdulrahman Al-Warthan, King Saud University**, for providing analysis for spectral measurements (Infrared and ^{1}H-NMR). Many thanks are also due to King Abdulaziz University, Department of Chemistry, and King Fahad Center for research at Jeddah for chemical analyses.

Finally, I send my supplication to my late father, **Mohammed A. Al-Ashqar**, may Allah bless him, who used to support me with his encouragement and love. Also, I thank very much my mother for her support and supplication while the work in progress.

S. M. A. Al-Ashqar

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INTRODUCTION

Tribochemistry:

Tribochemistry deals with the relations between mechanical work and mass transformation. The results can be found in various forms throughout nature and in human activity. They are so well known that they are mostly accepted without further consideration.

A reversal of the question shows the problems. What expenditure is needed to exclude chemical influences occurring during the mechanical interaction of one solid upon another? The experimental difficulties here are very great. It is desirable that highly pure solids mutually influence their structures upon application of mechanical work without causing more than mixed phases in solid or liquid state.

In the last century, Ostwald(1) had pointed out that a field of research should also belong to the effect of mechanical energy on chemical reactions. At that time, this field, which called "mechanochemistry", was virtually unexplored so that Ostwald was not able to say anything on the independent character and the importance of this field of chemistry.

In 1892 and 1894, two papers(2) have been published by Carey-Lea describing how mechanical could initiate chemical reactions. He could easily decompose $HgCl_2$ into it's components by triturating in a mortar. Since, this substance sublimes undecomposed into it's components upon heating, the

local heating was excluded by Carey-Lea as the cause of the initiation of the reaction. The silver halides also melt undecomposed at red heat, whereas under the influence of a small shear stress a partial decomposition takes place accompanied by the formation of metal(2). At the beginning of the last century, Parker conducted double reactions between simple salts influenced by frictional stress. He regarded the heat developed locally under friction as the cause of the release of this reaction(3).

In 1920, Tamman studied the changes in solid reactivity caused by mechanical treatment. He found that not all the mechanical energy is transformed into heat but from 5 to 15% of the expended energy remains in the metal as potential energy and increases the thermodynamic potential of the solid. As a consequence of the treatment a displacement of the thermodynamic potential and a significant increase of the dissolution velocity occurs(4).

In the subsequent three decades, Fink(5) and Bowden and Tabor(6) in particular, investigated oxidation reactions of metal and decomposition reactions under conditions of rolling and sliding frictions. Thus during the rolling friction of iron rolls on the stressed surface tarnishing layers come into existence within a few minutes, which without mechanical stress would normally require about 10^{17} years for their growth. Fink excluded the influence of temperature for the interpretation of this effect and discussed plastic deformation as a cause of the acceleration of the reaction(7).

By contrast, linking up with the concept of Parker, Bowden and Tabor developed the "hot-spot model" for the mechanical initiation of chemical reactions. They found that with, friction processes for $10^{-3} - 10^{-4}$ s, temperatures more than 1000 K can occur, and that these represent an important cause of mechanically initiated reactions.

In the fifties, Peters[8] investigated a whole series of inorganic reactions under the influence of mechanical energy, such as the decomposition and synthesis of carbonates, oxidation and reduction reactions as well as colour reactions for microanalysis. However, he disputed the role of temperature in initiating mechanically activated reactions, taking the attitude that only such reaction were to proceed where conditions for reactions are given from the thermodynamic point of view[8].

During the development of the foundations of this field of research, the real definitions also had to be adapted to the actual state of knowledge. The term "MECHANOCHEMISTRY" was coined by Ostwald[1] for this field of research. The following definition, generally accepted today, does justice to his concern to classify the individual fields of chemistry according to the kind of acting energy[9-11]:

"Mechanochemistry is a branch of chemistry dealing with the chemical and physicochemical changes of substances of all states of aggregation due to the influence of mechanical energy".

This field has been expanded in the most varied directions during the last decades. It is also includes for instance the

reactions released by cavitations in liquids, the shock wave reactions in gases, etc.

Mechanical influence plays a special part with regard to chemical reactions where at least one solid component is involved. The chief among these are reactions that occur with milling stress and friction, lubrication and abrasion.

The term "TRIBOCHEMISTRY" with the following definition has been coined for this special field(11-12) :

"Tribochemistry is a branch of chemistry dealing with the chemical and physicochemical changes of solids due to the influence of mechanical energy".

A great number of studies of the applications of tribochemistry in technology have been published(13-14). Tribochemical reactions have become important in the chemical, metallurgical and building industries and have led to the introduction of a number of tribochemical procedures to technology.

Recently, in the field of organic chemistry, it was reported that indole underwent solid state Michael addition reaction with α,β-unsaturated carbony1 compounds by which a series of compounds containing three different heterocyclic groups binding to one carbon atom were obtained. In the presence of Lewis acid, indole could undergo the solid state condensation reaction with aromatic ketones and aldehydes or quinines. The solid state reaction showed higher selectivity and yield than solution reaction. The structures of products were identified by

elemental analysis, IR, ^{1}H-NMR, mass spectra, and X-ray crystal analysis[15].

Also, a number of organic and organometalic aldehydes had been converted into optically active oxazolindines by solid state reactions with (-)-ephedrine and (+)-pseudoephedrine. The stereo selectivity of the solid state reaction is compared with that in boiling ethanol solution[16].

In the field of coordination chemistry, metal complexes may be synthesized by solid state reactions. Also, it had been reported that the solid state reaction between $La(OAc)_3.3/2H_2O$ and 8-hydroxyquinoline (oxine) was studied at low heating temperature. The metal complex with the formula $La(oxine)_3$ was synthesized by one step solid state reaction at 60 °C and the product was characterized by elemental analysis, IR, XRD, photocaustic spectra and fluorescence spectra[17].

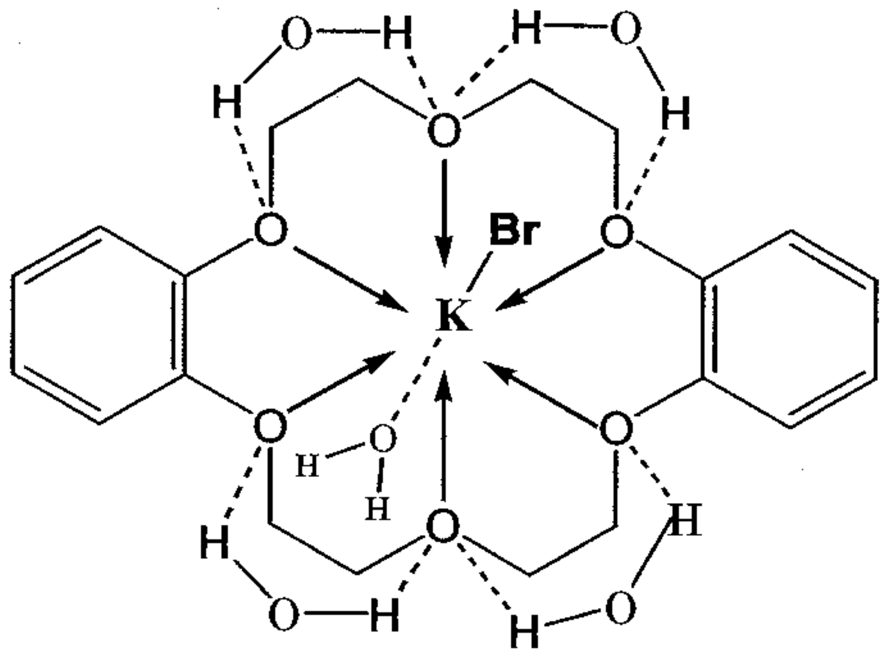
Also, the complexes, $[Cu(L_1)(PPh_3)_2I](1)$ and $[Cu(L_2)(PPh_3)_2Br](2)$, where L_1=2-[(4-hydroxyphenylmethane)] hydrazine carbothioamine, L_2=2-[2-hydroxyphenylmethane)] hydrazine carbothioamine, were obtained by the solid state reaction of L, CuX and PPh_3 and characterized by elemental analysis, IR, and UV-Vis. Spectroscopy. The crystal structure had been determined by single crystal X-ray diffraction. The Cu-atom coordinated tetrahedral by two P atoms from PPh_3, one halogen atom and one S atom from the ligand which acting as monodentate one. In complex(1), the Cu-S bond length was 2.402 Å while it was 2.3779 Å in complex(2) where that change is due to the different in crystal structure[18].

Three pentanuclear Cu(II) complexes, $[Cu_5(OMe)_2(CF_3COO)(PehP)_6Cl]$(1), $[Cu_5(OMe)_2(CF_3COO)(PehP)_6(NO_3)]$(2), and $[Cu_5(OH)(CF_3COO)_3(PehP)_6]$(3), had been prepared by the solid state reaction of hydrated Cu(II) nitrate with sodium salt of the ligand, 6-(phenylethenyl)-2-pyridine (HPehP), in the presence of CF_3COONa. Crystal structure at 220 K of complexes(1-3) revealed capped butterfly arrangements of the five Cu atoms. Mass spectroscopic studies of complexes(1-3) showed fragmentation patterns consistent with the observed structure while magnetic studied of the complexes indicated antiferromagnetic exchange coupling with the five copper cores and S = 1/2 ground state for all compounds(19).

A new heterometalic pentanuclear cluster, $[MS_4Cu_4(dppm)_4](PF_6)_6$, where M = W, Mo; dppm = bis (diphenylphosphino) methane, had been synthesized by the reaction of $(NH_4)_2(MS_4)$, dppm and $[Cu(CH_3CN)_4](PF_6)$ in the solid state at 110 °C. The X-ray studies showed that, in the structure of the direction of the two compounds, the central tetrahedral MS_4 core is enclosed by a sixteen-member heteroatom ring composed of four copper atoms and four dip molecules(20).

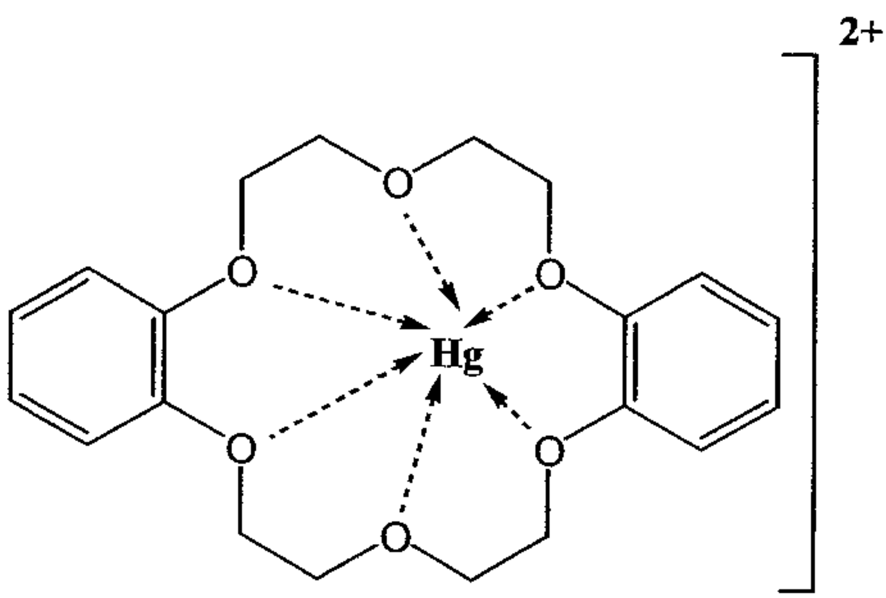
Recently, a spectroscopic study of some complex compounds derived from the tribochemistry reactions of KBr and HgX_2 (X = Cl, Br, I and CN) with some crown ethers (DC18C6 and DB18C6) was carried out(21). The tribochemistry reactions in these studies were carried out by mixing, girding in agate mortar and pressing with a pressure of 5-15 tons/cm^2 for

5 mins., of the ligands and metal salts. The reaction of KBr and crown ethers under different pressures (5, 10 and 15 tons/cm^2) in the solid state, during the preparation of KBr discs for IR measurements, is considered as an example for tribochemistry reactions. By comparison between the spectra of ligands in KBr and Nujol mull, the results indicated the formation of new complex compounds during the preparation of KBr discs with DB18C6 and that new complex had been isolated and characterized by chemical analysis[21] (structure 1).



(structure 1)

Also, by the same technique using tribochemistry reaction, the HgX_2 (X = Cl, Br, I and CN) complexes derived from some crown ethers (DC18C6 and DB18C6) were prepared. The HgX_2 complexes structures were characterized by elemental analysis, IR and ^{1}H-NMR, spectroscopic measurements. The results indicated that the HgX_2 complexes which prepared by tribochemistry reactions were identical to those of HgX_2 complexes prepared by conventional chemical methods (in solution)(22) (structure 2). The shifts in band positions of IR and ^{1}H-NMR spectra, were taken as evidence for the participation of oxygen atoms in bonding. The strength of bond is arranged as $Hg(CN)_2$ > $HgCl_2$ > $HgBr_2$ > HgI_2 in the complexes of both crown ethers (21).



(structure 2)

It was found that the tribochemistry reactions were used to prepare new solid complexes of Hg(II) and K^+ with some crown ethers (DC18C6 and DB18C6). This method is considered as an easy and economic method which can be generalized for other crown ethers and for other metal ions[21].

Novel Cu(I) and Cu(II) complexes derived from the tribochemistry reactions of $[Cu(GT)Cl_2(H_2O)_2(EtOH)]Cl.H_2O$ with KBr, KI and CaI_2 were isolated and characterized by Mostafa et. al.[23]. The reactions of KI and/or CaI_2 with $[Cu(GT)Cl_2(H_2O)_2(EtOH)]Cl.H_2O$ in the solid state were accompanied by colour change, reduction of Cu(II) to Cu(I) and substitution of the chloride by iodide ions. Also, the tribochemistry reaction of KBr with the Cu(II)-GT complex was accompanied by change in colour, substitution of chloride by bromide ions but reduction had occurred. All the isolated solid complexes were characterized by spectral (UV-Vis., IR, ^{1}H-NMR), magnetic and thermal measurements. The effect of the variation of the ratio between alkali and/or alkaline earth metals (KI , KBr and CaI_2) and the Cu(II)-GT complex were investigated.

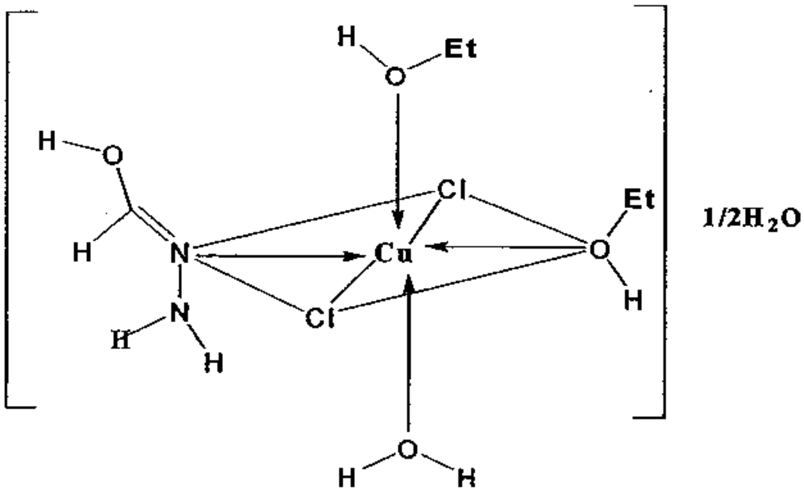
The authors[23] showed that KBr were reacted with different kinds of Cu(II) complexes, especially these containing chloride ions, during grinding and compressing to get the discs for IR measurements. This reaction was accompanied by substitution of chloride by bromide ions and no reduction was occurred. On using KI and/or CaI_2, instead of KBr, the Cu(II) complexes were reacted also where this reaction was accompanied by

substitution and reduction of Cu(II) to Cu(I). All these foundations were confirmed that the use of KBr, KI and/or CaI_2 during the IR measurements had led to misleading results. The only exception for that is the use of KBr with complexes containing the same anion, i.e., bromide ion. Also, the authors[(23)] were explained the reduction and substitution on the basis of a special mechanism. Moreover, the results showed that the isolated solid complexes were diamagnetic in nature except the complex isolated using KBr indicating the presence of square – planar configuration for these isolated from KI and CaI_2 while an octahedral structure for the bromide complex. Finally, the effect of DMSO and time on the Cu(I) complexes were explained.

Mostafa et. al.[(24)] were studied the tribochemical reactions of KBr, KI and CaI_2 with $[Cu(L)Cl_2(EtOH)_{3/2}(H_2O)]^1/_2H_2O$ (L = formylhydrazine). The isolated novel Cu(I) and Cu(II) complexes were characterized by elemental analyses, spectral (UV-Vis., IR, ^{1}H-NMR) and magnetic measurements. The spectral and magnetic results suggested a distorted-octahedral geometry for the Cu(II) complexes with a tetrahedral geometry around the Cu(I) ion. The non-stoichiometric structure of $[Cu_{1.7}(L)I_{1.7}(EtOH)_{½}]$ was discussed. The authors[(24)] indicated the failure of using KBr as a mulling agent, for many complex compounds, during IR measurements.

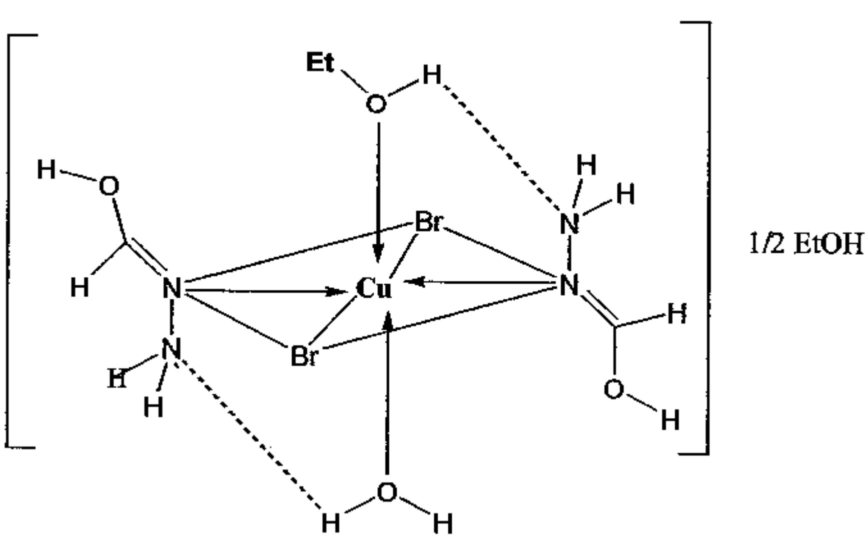
All the results (spectral and magnetic) for the complex, $[Cu(L)Cl_2(EtOH)_{½}(H_2O)]^1/_2H_2O$, suggested the existence of a distorted-octahedral geometry around the Cu(II) ion in which

the two chloride ions are mainly exist in a trans-position as shown in structure 3.



(structure 3)

A similar structure was proposed for the complex, $[Cu(L)_2Br_2(EtOH)(H_2O)]\frac{1}{2}EtOH$, with the existence of hydrogen bonding as shown in structure 4.



(structure 4)

Ru(III) complexes derived from the tribochemical reactions of $[Ru(GT)Cl_3(H_2O)]Cl.EtOH$ with KBr and KI were isolated and characterized by Mostafa et. al.[(25)]. The results showed that the reaction of KBr and KI with $[Ru(GT)Cl_3(H_2O)]Cl.EtOH$ in the solid state were accompanied by colour change and substitution of the chloride by bromide and/or iodide ions but no reduction of Ru(III) were occurred. The isolated solid complexes were characterized by elemental analyses, conductance, spectral (UV-Vis., IR), magnetic and thermal studies.

AIM OF WORK

Several years ago, we observed during the preparation of KBr discs for infrared measurements, that the colours of metal complexes were totally changed on grinding with KBr[22-25]. This process is known by us as tribochemical reactions and the field of this branch of chemistry is known as tritochemistry. Also, our earlier work[21] showed that some organic compounds such as crown ethers are reacted with KBr but no colour was changed. This means that the infrared spectra of complexes or organic compounds in KBr are not real. Also, the spectra of complexes and organic compounds are not characterized the original but it characterizes the reaction products with KBr. Consequentially, we advice to carry IR spectra of these compounds or complexes in Nujol, instead of KBr discs.

In this thesis, we extend our work to shed more light on this phenomenon especially for the complexes derived from some ligands containing N,O; N,S and N,O,S as donor atoms with KI. Also, one of our goal in this thesis is to prepare new complexes which can not be prepared by common chemical methods. Moreover, we have been able to prepare some Co(III) and Cu(I) complexes which are derived from the tribochemical reactions.

We began this field and we are still embarking on it to study it in details.

EXPERIMENTAL

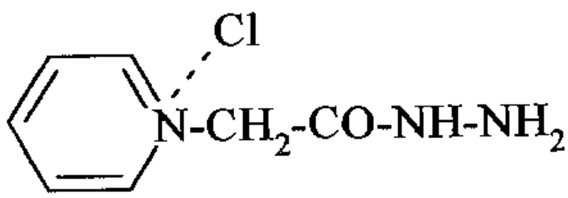
2.1. Reagents and Materials

All the chemicals used, phenyl isothiocyanate, ethyl isothiocyanate, 2-amino-3-picoline, 2-amino-6-picoline, 2-amino-3-hydroxypyridine, [(carboxymethyl) trimethylammonium chloride hydrazide] (G.T), [1-(carboxymethyl) pyridinium chloride hydrazide] (G.P), 2-aminophenol, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ and KI were of analytical grades, used without purification, and purchased from Aldrich. Also, the solvents (methanol, ethanol, chloroform, carbon tetrachloride, benzene, diethylether, dimethylformamide, dimethylsulphoxide and dichloroethane) were of BDH quality and used without purification.

2.2. Preparation of Ligands.

Eight ligands containing N,O; N,S and N,O,S as donor atoms were used for the preparation of solid complexes in this thesis. G.P. [1-(carboxymethyl)pyridinium chloride hydrazide] (structure 1) is the only ligand which was used for the preparation of solid complexes directly as supplied. The other seven ligands were prepared in laboratory and can be represented by the following structures (2-8):

i. [1-(carboxymethyl) pyridinium chloride hydrazide].

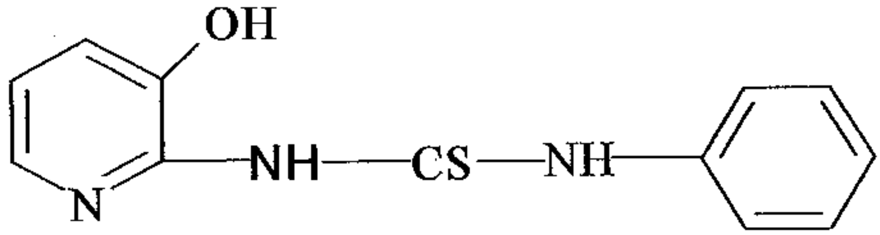


G.P. ($C_7H_{10}N_3OCl$; M.Wt. = 187.638)

(structure 1)

ii. N-(3-hydroxypyridine-2-yl)–N′-phenylthiourea (HPPTU).

The ligand (HPPTU, structure 2) was prepared by adding phenyl isothiocyanate (12 ml; 0.1 mol) dropwise with constant stirring to a solution of 2-amino-3-hydroxypyridine (11g, 0.1 mol) in absolute EtOH (200 ml). The reaction mixture was stirred at room temperature (25 °C) for 24 hrs. The pale brown crystals were obtained during stirring and the amount of crystals was increased with time of stirring. The excess solvent (EtOH) was removed by distillation. The product was recrystallized from absolute EtOH (m.p.,162 °C) and finally kept in a desiccator over anhydrous $CaCl_2$.

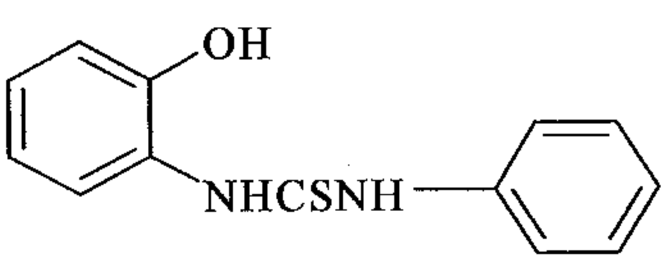


($C_{12}H_{11}N_3OS$; M.Wt. = 245.31)

(structure 2)

iii. N-2-(3-hydroxyphenyl)-N′-phyenylthiourea (3-HPPTU).

3-HPPTU (structure 3) was prepared by boiling under reflux a solution of 2-aminophenol (11g, 0.1 mol) and phenyl isothiocyanate (12 ml, 0.1 mol) in absolute EtOH (50 ml) for 3 hrs. The isolated white crystals were filtered off, recrystallized from EtOH (95%) and finally dried in a desiccator over anhydrous $CaCl_2$ (m.p., 138 °C).

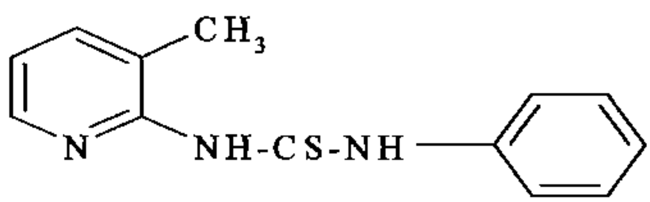


($C_{13}H_{12}N_2OS$, M.Wt. = 244.321)

(structure 3)

iv. N-2-(3-methylpyridyl)–N'–phenylthiourea (3-MPTU).

The ligand (structure 4) was prepared by boiling under reflux a solution of 2-amino–3–picoline (11g, 0.1 mol) and phenyl isothiocyanate (12 ml, 0.1 mol) in absolute EtOH (50 ml) for 1hr. The isolated white crystals were filtered off, recrystallized from absolute EtOH (m.p., 140 °C) and finally dried in a desiccator over anhydrous $CaCl_2$.

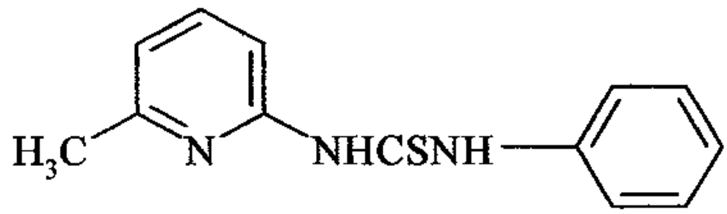


($C_{13}H_{13}N_3S$, M.Wt = 243.337)

(structure 4)

v. N-2-(6-methylpyridyl)–N'–phenylthiourea (6-MPTU).

This ligand (structure 5) was prepared using the same above procedure but we used in this method 2-amino-6-picoline. The white product was crystallized from EtOH (90%) and finally dried in a desiccator over anhydrous $CaCl_2$ (m.p., 188 °C).



($C_{13}H_{13}N_3S$, M.Wt = 243.337)

(structure 5)

vi. N-{[(allylamino)thioxomethyl]hydrazinocarbonylmethyl} trimethylammonium chloride (ATHTC).

The ligand (structure 6) was prepared by boiling under reflux a solution of G.T (16.8 g, 0.1 mol) and allyl isothiocyanate (9.8 ml, 0.1 mol) in absolute EtOH (50 ml) for 2 hrs. The white product was filtered off, recrystallized from absolute EtOH and finally dried in a desiccator over anhydrous $CaCl_2$ (m.p., 196 °C).



($C_9H_{19}N_4OSCl$; M.Wt. = 266.806)

(structure 6)

vii. N-{[(ethylamino) thioxomethyl]hydrazinocarbonylmethyl} trimethylammonium chloride (ETHTC).

ETHTC (structure 7) was prepared by boiling under reflux a solution of G.T (16.8 g, 0.1 mol) and ethyl isothiocyanate (8.8 ml, 0.1 mol) in absolute EtOH (75 ml) for 2 hrs. The white crystals were filtered off, recrystallized from absolute EtOH and finally dried in a desiccator over anhydrous $CaCl_2$ (m.p., 210 °C).

$$\overset{Cl}{\ } \\ (CH_3)_3\text{-}\,N\text{-}CH_2CONHNHCSNHC_2H_5$$

($C_8H_{19}N_4OSCl$, M.Wt. = 254.795)

(structure 7)

viii. N{[(phenylamino)thioxomethyl]hydrazinocarbonylmethyl} pyridinium chloride (PTHPC).

This ligand (structure 8) was prepared by refluxing a solution of G.P (18.8 g, 0.1 mol) and phenyl isothiocyanate (12 ml; 0.1 mol) in absolute EtOH (100 ml) for 4 hrs. The product was filtered off, recrystallized from absolute EtOH and finally dried in a desiccator over anhydrous $CaCl_2$ (m.p.,194 °C) .



($C_{14}H_{15}N_4OSCl$; M.Wt. = 322.829)

(structure 8)

The solubilities and some physical properties of the ligands are listed in table 1.

2.3.1. Preparation of Solid Complexes by Conventional Chemical Method.

Cobalt(II) and copper(II) complexes were prepared by a conventional chemical method, where 0.1 mol of metal salts ($CoCl_2.6H_2O$ and $CuCl_2.2H_2O$) in EtOH (50 ml) were added drop by drop with constant stirring to 0.2 mol of the ligands under investigation in 50 ml EtOH. The reaction mixture was refluxed on a hot plate for 1 hr and the product was filtered off hot. The isolated solid complexes were washed successively with EtOH and diethylether and preserved in vacuum desiccator over anhydrous $CaCl_2$. Different complexes of Co(II) and Cu(II) with different ratios, 1:1, 1:2 and 1:3 (M:L), have been isolated and characterized by conventional physical and chemical methods. The only pure forms of the isolated solid

complexes were used to prepare the solid complexes using the technique of tribochemical reactions. The solubilities and some physical properties of the solid complexes are listed in table 2.

2.3.2. Preparation of Complexes by Tribochemical Reactions With KI.

The pure solid Co(II) and Cu(II) complexes, prepared by chemical method, were added to KI with ratio 1:3 (complex : KI) by weight. The reaction mixture was grinded in agate mortar for 2 hrs. During the grinding process, we observed that the colours of the original complexes were changed dramatically and became deep in colours (brown or red). A mixture of MeOH/EtOH (85: 15) was then added to the product and the reaction mixture was boiled for 15 mins. The reaction mixture was then further refluxed on a hot plate for 2 hrs. The precipitate was filtered off hot, washed several times with 100 ml of a mixture of EtOH/MeOH (80: 20) and finally the complexes were kept in a vacuum desiccator over $CaCl_2$. The solubilities and some physical properties of the solid complexes are shown in table 3.

2.4. Analyses of Complexes.

In order to suggest the correct formulae of the isolated solid complexes, elemental analyses (C, H, N, S) and metal contents were carried out according to the standard methods:

1. Carbon, hydrogen, nitrogen and sulphur contents were performed at the Microanalytical Unit at **King Fahd for Medical Research Center, Jeddah,** using Perkin-Elmer Microanalyzer model 2400.
2. Metal ions (Cu^{2+} and Co^{2+}) were determined complexometrically using 0.01M EDTA and xylenol orange as indicator[(26-27)].
3. Copper(I) was determined gravimetrically as CuSCN[(28)].
4. Cobalt(III) was determined gravimetrically using nitroso-2-naphthol as a reagent[(28)] and by atomic absorption spectrophotometry technique.

The results of elemental analyses of the ligands and metal complexes are listed in tables 4-6 which include the percentage of the constituents as calculated on the basis of the suggested formulae.

2.5. Preparation of Solutions.

2.5.1. EDTA Solution.

A solution of the disodium salt of ethylenediamine tetracetic acid (0.01 M) was prepared and standardized against $MgSO_4.7H_2O$ (0.01M) using Eriochrome black T as indicator[(28)].

2.5.2. Lead Nitrate Solution.

A solution of anhydrous lead nitrate (0.01 M) was prepared and standardized against EDTA solution (0.01M) and xylenol orange as indicator[(28)].

2.6. Working Procedure.

2.6.1. Conductance Measurements.

Molar conductance measurements of the solid complexes (10^{-3} M) in DMF were obtained with a conductivity bridge YSI model 32. The calculation was determined by applying the following equation:

$$\Lambda_m = \frac{1000 \times K \times m}{R \times M} \longrightarrow 1$$

Λ_m = molar conductance in $\Omega^{-1}.cm^{2}.mol^{-1}$.

M = molecular weight.

m = weight (grams) of solute per 10 ml of DMF.

R = resistance of solution in ohms.

K = cell constant (1.34).

2.6.2. Infrared Spectra.

Infrared spectra of the ligands as well as the solid complexes were measured using KBr discs and/or Nujol mull on a Mattson 5000 FTIR spectrometer. The frequency reading was calibrated with a polystyrene film at Mansoura University, Egypt.

2.6.3. Electronic Spectra.

The electronic spectra of the isolated solid complexes were recorded in Nujol mull on Unicam UV/Vis. spectrometer model V2-30 at Mansoura University, Egypt.

2.6.4. Magnetic Susceptibility Measurements.

Magnetic moments were carried out on Sherwood magnetic balance. The calculations were evaluated by applying the following equations:

(2) $$\chi_g = \frac{C \times \ell \times (R - R_0)}{M \times 10^9} \longrightarrow 2$$

(3) $$\chi_M = \chi_g \times M.\ Wt \times 10^{-3} \longrightarrow 3$$

M.Wt. = Molecular weight.

(4) $$\mu_{eff.} = 2.84 \sqrt{\chi_M \times T} \longrightarrow 4$$

χ_M = The mass susceptibility per gram sample.

C = The calibration constant of the instrument (1.087).

ℓ = The sample length in cm.

R = The balance reading for the sample and tube.

R_o = The balance reading for the tube only.

M = The weight of the sample in gram.

T = Absolute temperature (273 + t).

2.6.5. ^{1}H -NMR Spectra.

^{1}H-NMR spectra of the ligands and the isolated solid complexes in d_6-DMSO were recorded on Jeol NMR Spectrometer (400 MHz), eclipse 400, Japan at **Chemistry Department, Faculty of Sciences and Research Center at King Saud University, Riyadh, KSA.**

Table 1: Solubilities and some physical properties of the ligands.

Compound	Colour	M.p., °C	Solubility						
			H_2O	EtOH	$CHCl_3$	CCl_4	C_6H_6	DMF	DMSO
Girard's P ($C_7H_{10}N_3OCl$)	yellowish-white	201-203	S	p.s	i.s	i.s	i.s	s	s
HPPTU ($C_{12}H_{11}N_3OS$)	Pale- brown	162	p.s	p.s	i.s	i.s	i.s	s	s
3-HPPTU ($C_{13}H_{12}N_2OS$)	Wbite	138	i.s	p.s	i.s	i.s	i.s	s	s
3-MPTU ($C_{13}H_{13}N_3S$)	White	140	i.s	p.s	i.s	i.s	i.s	s	s
6.MPTU ($C_{13}H_{13}N_3S$)	White	188	i.s	p.s	i.s	i.s	i.s	s	s
ATHTC ($C_9H_{19}N_4OSCl$)	White	196	p.s	p.s	i.s	i.s	i.s	s	s
ETHTC ($C_8H_{19}N_4OSCl$)	White	210	p.s	p.s	i.s	i.s	i.s	s	s
PTHPC ($C_{14}H_{15}N_4OSCl$)	White	194	p.s	p.s	i.s	i.s	i.s	s	s

i.s = insoluble p.s = partially soluble s = soluble

Table 2. Solubilities and some physical properties of some Cu(II) and Co(II) complexes prepared by conventional chemical method.

Compound	Colour	M.p., °C	Solubility						
			H_2O	EtOH	$CHCl_3$	CCl_4	C_6H_6	DMF	DMSO
$[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$	blue	224 d	s	i.s	i.s	i.s	i.s	s	s
$[Cu_2(C_7H_{10}N_3O)_2Cl_2]Cl_4.2EtOH$	Yellowish- green	228 d	s	i.s	i.s	i.s	i.s	s	s
$[Co(C_7H_{10}N_3O)_2(H_2O)_2]Cl_2.4H_2O$	violet	184 d	s	i.s	i.s	i.s	i.s	s	s
$[Cu_2(C_7H_9N_3O)_2Cl_2(H_2O)_2(EtOH)_2]Cl_2$	green	135 d	s	i.s	i.s	i.s	i.s	s	s
$[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$	blue	284 m	s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$	Yellowish- green	224 m	s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$	Yellowish- green	171 m	p.s	i.s	i.s	i.s	i.s	s	s
$[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$	brown	146 m	p.s	i.s	i.s	i.s	i.s	s	s
$[Co(C_{13}H_{13}N_3S)Cl_2]½ H_2O. ½ EtOH$	petrol	196 m	s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{13}H_{13}N_3S)_2Cl.H_2O]Cl$	olive-green	310 d	p.s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{13}H_{13}N_3S)Cl_2]$	Yellowish- green	168 d	p.s	i.s	i.s	i.s	i.s	s	s
$[Co(C_{13}H_{13}N_3S)_2]Cl_2.½ H_2O$	blue	189 m	s	i.s	i.s	i.s	i.s	s	s
$[Co(C_9H_{19}N_4OS)_2]Cl_4.4H_2O$	blue	178 m	p.s	i.s	i.s	i.s	i.s	s	s
$[Co(C_9H_{19}N_4OS)Cl_2]Cl$	blue	212 m	s	i.s	i.s	i.s	i.s	s	s
$[Co(C_8H_{17}N_4OS)H_2O]Cl.2H_2O.½EtOH$	blue	180 m	s	i.s	i.s	i.s	i.s	s	s
$[Co(C_{14}H_{15}N_4OS)Cl_2]Cl.2EtOH$	petrol	176 m	s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{14}H_{15}N_4OS)Cl_2.H_2O]Cl.1/2EtOH$	deep green	154 m	s	i.s	i.s	i.s	i.s	s	s

Table 3: Solubilities and some physical properties of some copper and cobalt complexes prepared by tribochemical reaction.

Compound	Colour	M.p., °C	Solubility						
			H_2O	EtOH	$CHCl_3$	CCl_4	C_6H_6	DMF	DMSO
$[Co(C_7H_{10}N_3O)I_2.I.½ H_20.½ EtOH]I.H_2O$	selmon	220 m	s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_7H_{10}N_3O)I_2] [CuI_2. ½EtOH]2H_2O$	yellowish- green	250 d	p.s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_7H_{10}N_3O)I_2] [CuI_3. ½ EtOH]$	yellowish- brown	270 d	p.s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{12}H_{11}N_3OS)I.H_2O]4H_2O$	yellowish- brown	254 m	p.s	i.s	i.s	i.s	i.s	s	s
$[Co(C_{12}H_{11}N_3OS)_4.I_2]I$	green	154 m	s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{13}H_{12}N_2OS)I.H_2O] ½ H_2O$	pale yellow	200 d	p.s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{13}H_{13}N_3S)_3]I_2. ½H_2O$	petrol	>300	p.s	i.s	i.s	i.s	i.s	s	s
$[Cu(C_{13}H_{13}N_3S)(H_2O).I]4H_2O$	white	>300	p.s	i.s	i.s	i.s	i.s	s	s
$[Co(C_{13}H_{13}N_3S)(H_2O)_4]I_3.6H_2O$	turquoise	180 d	p.s	i.s	i.s	i.s	i.s	s	s
$[Co(C_9H_{19}N_4OS).I_3.½EtOH]I$	brown	192 m	s	i.s	i.s	i.s	i.s	s	s
$[Co_2(C_9H_{19}N_4OS).I_4]I.EtOH$	blue	>300	s	p.s	i.s	i.s	i.s	s	s
$[Co(C_8H_{18}N_4OS).I_2.3/2EtOH] I$	petrol	204 m	s	p.s	i.s	i.s	i.s	s	s
$[Co(C_{14}H_{15}N_4OS).I_2. H_2O]I.3H_2O$	deep brown	224 d	s	p.s	i.s	i.s	i.s	s	s
$[Cu(C_{14}H_{15}N_4OS).I]I.7H_2O$	yellowish-brown	170 m	s	i.s	i.s	i.s	i.s	s	s
$[Cu_2(C_8H_{18}N_4OS).I(H_2O)_3]I.H_2O$	white	220 d	s	i.s	i.s	i.s	i.s	s	s
$[Co_2(C_8H_{17}N_4OS).I_4(EtO)_2(H_2O)_2]I. ½EtOH$	blue	230 d	s	i.s	i.s	i.s	i.s	s	s

RESULTS AND DISCUSSION

3.1. Preparation of Metal Complexes.

3.1.1. Preparation of Co(II) and Cu(II) Complexes by Conventional Chemical Method.

The reactions of the ligands under investigation, (G.P., HPPTU, 3-HPPTU, 3-MPTU, 6-MPTU, ATHTC, ETHTC and PTHPC), with the metal salts ($CoCl_2.6H_2O$, $CuCl_2.2H_2O$) in absolute EtOH afford several complexes with different molar ratios (M:L). The ratio of metal complexes depends mainly on the method of addition (addition of metal salt to ligand or vice versa), type of solvent used, nature of metal and ligand (strength as Lewis acid or Lewis base) as well as the pH of solution during complex formation. Doubtless the time of reflux as well as the temperature of the reaction mixture during complex formation have also great effects on the structure and ratio of the isolated metal complexes. Elemental analyses, spectral and magnetic measurements suggest the chemical formulae as well as the stereochemistry of the isolated metal complexes. The results of the elemental analyses of the ligands and metal complexes prepared by conventional method are shown in Tables 4 and 5. Comparison of the analyses for the calculated and found ratios indicates that the composition of the isolated solid complexes coincide with the proposed formulae. Also, the results of molar conductivities for the solid complexes in DMF indicate that the complexes are either neutral or cationic in nature.

Table 4. Elemental analyses of the ligands.

Compound	% Calcd.				% Found			
	C	H	N	S	C	H	N	S
$C_{12}H_{11}N_3OS$; HPPTU	58.8	4.5	17.1	13.1	58.3	4.4	16.9	13.0
$C_{13}H_{12}N_2OS$; 3-HPPTU	63.9	5.0	11.5	13.1	63.7	5.0	11.3	13.0
$C_{13}H_{13}N_3S$; 3- MPTU	64.2	5.4	17.3	13.2	64.1	5.4	17.2	13.1
$C_{13}H_{13}N_3S$; 6 -MPTU	64.2	5.4	17.3	13.2	64.2	5.3	17.1	12.9
$C_8H_{19}N_4OSCl$, ETHTC	37.7	7.5	22.0	12.6	37.5	7.4	21.9	12.5
$C_9H_{19}N_4OSCl$, ATHTC	40.5	7.2	21.0	12.0	40.3	7.1	20.7	11.7
$C_{14}H_{15}N_4OSCl$, PTHPC	52.1	4.7	17.4	9.9	52.1	4.8	17.6	10.1

In order to shed more light on the metal complexes prepared by conventional chemical method, we obliged to classify the complexes into three categories to facilitate their studies. This classification involves N,O; N,S and N,O,S and can be represented as follows:

i. Ligand involves N and O as donor atoms, i.e., G.P.

ii. Ligands involve N and S as donor atoms, i.e., 3-MPTU and 6-MPTU.

iii. Ligands involve N, O and S as donor atoms, i.e., HPPTU, 3-HPPTU, ATHTC, ETHTC and PTHPC.

i. Ligand Involves N and O as Donor Atoms, i.e., G.P.

Different chemical structures have been isolated from the reaction of G.P. with Co(II) and Cu(II) salts. All the isolated complexes are cationic in nature and have 2:2 and/or 1:2 (M:L) ratio. The IR spectra of the complexes, $[Cu_2(C_7H_{10}N_3O)_2Cl_2]Cl_4.2EtOH$, $[Cu_2(C_7H_9N_3O)_2Cl_2(H_2O)_2(EtOH)_2]Cl_2$, $[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$ and $[Co(C_7H_9N_3O)_2(H_2O)_2]Cl_2.4H_2O$, suggest that the first and third complexes were separated in the keto form while the second and fourth complexes are existed in the enol form. Also, the results indicate that the Cu(II) complexes tend to polymerize on long standing (one week) at room temperature, meanwhile the

Co(II) complexes resist and remain unpolymerized even on long standing at room temperature (25 °C).

The first Cu(II) complex, $[Cu_2(C_7H_{10}N_3O)_2Cl_2]Cl_4.2EtOH$, was prepared by adding 0.01 mol (1.88 g) of G.P. in EtOH (25 ml) to 0.01 mol of $CuCl_2.2H_2O$ (1.7 g) in EtOH. The reaction mixture was heated under reflux for 1h. The reaction mixture was changed to a polymer by heating but on cooling the complex changes again to yellowish-green powder (m.p.,228 °C). On long standing at room temperature (25 °C) the complex changes to a brown polymer.

The second complex, $[Cu_2(C_7H_9N_3O)_2Cl_2.(H_2O)_2(EtOH)_2]Cl_2$, was obtained by a rapid adding of 0.01 mol of $CuCl_2.2H_2O$ (1.7 g) in 25 ml EtOH to 0.02 mol of G.P. (3.8 g) in 50 ml EtOH. During the rapid addition of $CuCl_2$ solution to the G.P solution, a gas was evolved and on testing this gas by ammonia solution a white cloud was formed. This indicates that the enolization process is occurred with evolution of HCl gas. The product has a green colour (m.p.,135 °C) and changes to yellowish-brown polymer on long standing at room temperature (25 °C).

The third complex with the general formula, $[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$, was prepared by adding 0.01 mole of $CoCl_2.6H_2O$ (2.4 g) in 25 ml EtOH to 0.01 mol of G.P (3.8 g) in 50 ml EtOH. The addition of metal salt solution was continued for two hrs accompanied by constant stirring until a blue product was formed. The complex was filtered hot followed by washing several times with EtOH and diethylether, respectively. In case

of the fourth complex, $[Co(C_7H_9N_3O)_2H_2O]Cl_2.4H_2O$, the same amounts of reactants were used as the previous cobalt complex but the Co(II) solution was added at once. Also, we observed the evolving of HCl gas during this reaction followed by precipitation of a violet complex (m.p., 184 °C).

ii. Ligands Involve N and S as Donor Atoms, i.e., 3-MPTU and 6-MPTU.

Four different complexes with the general formulae, $[Co(C_{13}H_{13}N_3S)Cl_2]½H_2O.½EtOH$, $[Cu(C_{13}H_{13}N_3S)_2Cl.H_2O]Cl$, $[Cu(C_{13}H_{13}N_3S)Cl_2]$ and $[Co(C_{13}H_{13}N_3S)_2]Cl_2.½H_2O$ have been isolated from the reaction of 3-MPTU and/or 6-MPTU with $CoCl_2.6H_2O$ and $CuCl_2.2H_2O$ in EtOH. The results indicate the non-ionic nature of the first and third complexes while the second and fourth complexes have cationic nature.

The first complex, $[Co(C_{13}H_{13}N_3S)Cl_2]½H_2O.½EtOH$, was prepared by adding 0.01 mol of $CuCl_2.2H_2O$ (1.7 g) in EtOH (25 ml) to 0.02 mol of 3-MPTU (4.8 g) in 100 ml. EtOH. The reaction mixture was heated under reflux on a hot plate for 1 hr. The petrol product (m.p., 196 °C) was filtered off hot and washed successively with hot EtOH followed by diethylether.

The second complex, $[Cu(C_{13}H_{13}N_3S)_2Cl.H_2O]Cl$, was prepared by adding 0.01 mol of $CuCl_2.2H_2O$ (1.7 g) in EtOH (25 ml) to 0.02 mol of 3-MPTU (4.8 g) in 100 ml EtOH. The reaction mixture was heated under reflux on a hot plate for 1 hr.

The olive- green product (m.p., 310 °C) was filtered off hot and washed successively with hot EtOH followed by diethylether. The third complex, $[Cu(C_{13}H_{13}N_3S)Cl_2]$, was prepared in the same way as that used for preparing the first complex. The complex has a yellowish-green colour (m.p., 168 °C). On the other hand, the procedure for preparing of the fourth complex, $[Co(C_{13}H_{13}N_3S)_2]Cl_2.\frac{1}{2}H_2O$, follows the same way as that reported for the second one. The complex has a blue colour (m.p., 189 °C).

iii. Ligands Involve N,O and S as Donor Atoms, i.e., HPPTU, 3-HPPTU, ATHTC, ETHTC and PTHPC.

All the five ligands of this type contain N,O and S within its structures. In spite of the presence of these three donor atoms, the ligands coordinate in a bidentate manner *via* N and O atoms only except the complexes with the general formulae, $[Cu(C_{14}H_{15}N_4OS)Cl_2.H_2O]Cl.1/2EtOH$ and $[Co(C_8H_{18}N_4OS)Cl]Cl.2H_2O.1/2EtOH$ in which the ligands (PTHPC, ETHTC) behave in a tridentate fashion *via* N,O and S atoms. The first two ligands (HPPTU and 3-HPPTU) form four different complexes with the general formulae, $[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$, $[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$, $[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$ and $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$.

The first two complexes, $[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$ and $[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$, have been synthesized from

the reactions of and 3-HPPTU with $CoCl.6H_2O$ and $CuCl_2.2H_2O$ in EtOH. The results indicate that the complexes are cationic in nature except the former complex which is neutral. Also, the data suggest that the ligands coordinate in a bidentate nature and in the keto form except the former complex which the ligand (HPPTU) coordinates to the Co(II) ion in the enol form.

The first complex, $[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$, was prepared by adding 0.01 mol of HPPTU (2.5 g) in EtOH (50 ml) to a solution of 0.01 mol of $CoCl_2$. $6H_2O$ (2.4 g) in EtOH (25 ml) with constant stirring. The reaction mixture was refluxed on a hot plate for 2 hrs. The blue product (m.p., 284 °C) was filtered off hot and washed successively with hot EtOH followed by diethylether. In this case we observed the evolution of HCl gas during complex formation indicating that the deprotonation process was occurred *via* the OH group.

The second complex, $[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$, was prepared by adding 0.01 mol of $CuCl_2.2H_2O$ (1.8 g) in EtOH (25 ml) to a solution of HPPTU (5 g) in 100 ml EtOH. The reaction mixture was refluxed on a hot plate for 1 hr. The yellowish-green product (m.p., 224 °C) was filtered off hot and washed with EtOH and diethylether.

The third and the fourth complexes derived from 3-HPPTU with the general formulae, $[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$ and $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$, were prepared by adding 1:3 and 1:2 (M:L) ratios, respectively. The same procedure was used for preparation of these complexes as above. The colours of

these complexes are yellowish-green (m.p., 171 °C) and brown (146 °C), respectively. The results indicate that the colours of these complexes remain unchanged on long standing at room temperature (25 °C).

The remaining five complexes derived from ATHTC, ETHTC and PTHPC have the following formulae, $[Co(C_9H_{19}N_4OS)_2]Cl_4.4H_2O$, $[Co(C_9H_{19}N_4OS)Cl_2]Cl$, $[Co(C_8H_{18}N_4OS)Cl]Cl.2H_2O.1/2EtOH$, $[Co(C_{14}H_{15}N_4OS)Cl_2]Cl.2EtOH$ and $[Cu(C_{14}H_{15}N_4OS)Cl_2.H_2O]Cl.1/2EtOH$. All the metal complexes were prepared in a 1:1 (M:L) ratio except the former which was prepared in a ratio of 1:2 (M:L). The results indicate that all these complexes are ionic in nature. Also, the results show that the ligands coordinate to the metal ions in the keto form except the third complex, $[Co(C_8H_{18}N_4OS)Cl]Cl.2H_2O.1/2EtOH$, which the ligand behaves in the enol form. Moreover, the colours of all complexes remain unchanged on long standing at room temperature (25 °C). The melting points of the five complexes are 178, 212, 180, 176 and 154 °C, respectively.

Table 5. Elemental analyses and molar conductivities of metal complexes derived by conventional chemical method.

Compound	% Calcd.					% Found					Λ_m in
	C	H	N	S	M	C	H	N	S	M	DMF
$[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$	26.5	3.2	13.2	-	18.6	26.6	3.7	13.1	-	18.2	169.2
$[Cu_2(C_7H_{10}N_3O)_2Cl_2]Cl_4.2EtOH$	29.4	4.4	11.4	-	17.3	29.6	4.2	11.1	-	17.1	155.8
$[Co(C_7H_9N_3O)_2(H_2O)_2]Cl_2.4H_2O$	31.1	5.6	15.6	-	10.9	31.1	5.7	14.9	-	10.8	70.2
$[Cu_2(C_7H_9N_3O)_2Cl_2(H_2O)_2(EtOH)_2]Cl_2$	30.9	4.9	12.0	-	18.2	30.3	4.3	11.9	-	18.0	77.4
$[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$	43.2	3.6	11.6	8.9	16.3	43.6	3.2	11.2	8.4	16.1	9.3
$[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$	43.6	4.0	12.7	9.7	9.6	43.6	3.3	13.0	8.4	9.1	31.7
$[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$	50.8	4.6	9.1	10.4	6.9	50.4	4.2	10.2	9.6	6.3	66.3
$[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$	47.7	4.3	8.6	9.8	9.0	47.8	3.6	8.8	8.8	8.7	49.0
$[Co(C_{13}H_{13}N_3S)Cl_2]½\ H_2O.\ ½\ EtOH$	41.5	4.2	10.4	7.9	14.5	41.1	4.1	10.2	7.2	14.1	6.3
$[Cu(C_{13}H_{13}N_3S)_2Cl.H_2O]Cl$	48.9	4.4	13.2	10.0	9.9	48.1	4.0	13.7	9.8	9.6	33.7
$[Cu(C_{13}H_{13}N_3S)Cl_2]$	41.3	3.5	11.1	8.5	16.8	41.6	3.6	11.6	8.4	16.4	8.3
$[Co(C_{13}H_{13}N_3S)_2]Cl_2.½H_2O$	49.9	4.4	13.4	10.3	9.4	49.8	4.2	13.9	10.1	9.8	76.2
$[Co(C_9H_{19}N_4OS)_2]Cl_4.4H_2O$	29.4	6.3	15.2	8.7	8.0	28.6	6.2	15.0	8.5	8.0	145.5
$[Co(C_9H_{19}N_4OS)Cl_2]Cl$	27.3	4.8	14.1	8.1	14.9	26.8	4.8	14.0	8.0	14.7	38.6
$[Co(C_8H_{18}N_4OS)Cl]Cl.2H_2O.1/2EtOH$	26.5	6.2	13.8	7.9	14.5	26.5	6.5	14.3	7.9	14.1	40.1
$[Co(C_{14}H_{15}N_4OS)Cl_2]Cl.2EtOH$	39.7	5.0	10.3	5.9	10.8	39.0	5.2	10.6	6.2	10.4	40.4
$[Cu(C_{14}H_{15}N_4OS)Cl_2.H_2O]Cl.1/2EtOH$	36.2	4.0	11.2	6.4	12.8	35.9	3.4	12.6	6.7	13.4	38.1

3.1.2. Preparation of Metal Complexes by Tribochemical Reactions.

Generally, these complexes were prepared by grinding thoroughly the previous complexes, which were prepared by conventional chemical method (Table 2), with KI in a mortar. The ratio used for mixing the reactants is 1:3 (complex: KI). The novel metal complexes obtained were extracted from the product using a mixture of MeOH and EtOH (85/15, V/V). The isolated solid complexes were filtered off, washed several times with EtOH and diethylether, respectively.

Some observations and facts should be focused on this method of preparation before discussing the method in details. Firstly, the colours of the original complexes (Table 2) were totally changed on comparison to these isolated by tribochemical reactions (Table 3). Secondly, the colours of the complexes prepared by tribochemical reactions (Table 3) are not stable on long standing at room temperature (25 °C). Thirdly, most of the Cu(II) complexes are reduced to Cu(I) and few remain unchanged. On the other hand, few Co(II) complexes are oxidized to Co(III) while most of Co(II) complexes remain unchanged. Finally, the ligands containing chloride ions are totally substituted by iodide ions.

The results of elemental analyses for the metal complexes derived by tribochemical reactions are listed in Table 6.

To facilitate our discussion we will classify the complexes into four categories according to the mode of coordination:

1. Ligand acts in a monodentate manner, i.e., HPPTU.
2. Ligands act in a bidentate manner, i.e., G.P., HPPTU, 3-HPPTU, 3-MPTU, 6-MPTU and ATHTC.
3. Ligand acts in a tridentate manner, i.e., PTHPC.
4. Ligands act in a tetradentate manner toward two metal ions, i.e., ETHTC and ATHTC.

In order to shed more light on these four categories we will discuss each type separately and in details as follows:

3.1.2.1. Ligand Act in A Monodentate Manner, i.e., HPPTU.

The only complex of this type was isolated and characterized which has the following general formula,. (HPPTU).

This complex, $[Co(C_{12}H_{11}N_3OS)_4I_2]I$ was prepared by grinding 0.01 mol (3.3 g) of the original complex, $[Co(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$ with KI (13.2 g) in agate mortar until the mixture became homogeneous and deep in colour. A mixture of MeOH and EtOH (85/15 V/V) was added to the reactants and then the reaction mixture was stirred on a magnetic stirrer for 24 hrs at room temperature. The reaction mixture was filtered off, washed with EtOH (150 ml) and diethyl ether (100 ml) successively and finally the product was left to dry in a vacuum desiccator over anhydrous $CaCl_2$. The isolated solid complex, $[Co(C_{12}H_{11}N_3OS)_4I_2]I$, has a green colour (m.p., 154 ^{o}C). This complex is diamagnetic in nature, i.e., the original Co(II) complex is oxidized to Co(III).

3.1.2.2. Ligands Act as Bidentate, i.e., G.P, HPPTU, 3-HPPTU, 3-MPTU, 6-MPTU and ATHTC

The tenth complexes of the general formulae, $[Co(C_7H_{10}N_3O)I_2.½H_2O.½EtOH]I.H_2O$ (G.P.), $[Cu(C_7H_{10}N_3O)I_2][CuI_2.1/2EtOH]2H_2O$ (G.P.), $[Cu(C_7H_{10}N_3O)I][CuI_3.½EtOH]$ (G.P.), $[Cu(C_{12}H_{11}N_3OS)I.H_2O]4H_2O$ (HPPTU), $[Cu(C_{13}H_{12}N_2OS)I.H_2O]1/2H_2O$ (3-HPPTU), $[Cu(C_{13}H_{13}N_3S)_3]I_2.1/2H_2O$ (3-MPTU), $[Cu(C_{13}H_{13}N_3S)(H_2O)I]4H_2O$ (3-MPTU), $[Co(C_{13}H_{13}N_3S)(H_2O)_4]I_3.6H_2O$ (6-MPTU), $[Co(C_9H_{19}N_4OS)I_3.½EtOH]I$ (ATHTC), and $[Co(C_8H_{18}N_4OS)I_2.3/2EtOH]I$ have been isolated and characterized.

The former three complexes were prepared by mixing the corresponding complexes, which were prepared by conventional chemical method, $[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$, $[Cu_2(C_7H_9N_3O)_2Cl_2(H_2O)_2(EtOH)_2]Cl_2$ and $[Cu_2(C_7H_{10}N_3O)_2Cl_2]Cl_4.EtOH$, with KI. The reaction mixture was mixed thoroughly in agate mortar until the mixture became homogenous and deep in colour. The new complexes were obtained by adding a mixture of MeOH and EtOH (85/15), filtered off and finally dried in a vacuum desiccator over anhydrous $CoCl_2$. All the isolated solid complexes are paramagnetic in nature. Also, the colours of the former and latter are changed on long standing (two months) at

room temperature (25 °C) while the second complex remains unchanged.

The latter two complexes of this category with the general formulae, $[Cu(C_{12}H_{11}N_3OS)I.H_2O]4H_2O$ (HPPTU) and $[Cu(C_{13}H_{12}N_2OS)I.H_2O]1/2H_2O$ (3-HPPTU), were prepared by mixing the corresponding complexes, which were prepared by conventional chemical method, $[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]H_2O$ and $[Cu(C_{13}H_{12}N_2OS)]Cl_2.\ 3H_2O$, with KI in agate mortar until the mixtures became homogeneous and deep in colours. The complexes were obtained and extracted with 200 ml of a mixture of MeOH and EtOH followed by filtration and drying in a desiccator over anhydrous $CaCl_2$. The two isolated solid complexes are diamagnetic in nature and their colours are changed on long standing (two months) at room temperature (25 °C). This suggests that the two Cu(II) complexes are reduced to Cu(I).

The sixth and seventh complexes with general formulae, $[Cu(C_{13}H_{13}N_3S)_3]I_2.1/2H_2O$ (3-MPTU), $[Cu(C_{13}H_{13}N_3S)(H_2O).I]4H_2O$ (3-MPTU), were prepared by mixing the original complexes, $[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$ and $[Cu(C_{13}H_{13}N_3S)Cl_2$, with KI in a agate mortar until the mixtures became homogeneous and deep in colours. The solid complexes were obtained by extraction with 250 ml of a mixture of MeOH and EtOH followed by filtration and drying in a desiccator over anhydrous $CaCl_2$. The former complex is paramagnetic in nature and its colour remains unchanged on standing in air while the second complex is diamagnetic and its colour changes on long standing (two months).

The latter three complexes with the general formulae, $[Co(C_{13}H_{13}N_3S)(H_2O)_4]I_3.6H_2O$ (6-MPTU), $[Co(C_9H_{19}N_4OS)I_3.½EtOH]I$ (ATHTC), and $[Co(C_8H_{18}N_4OS)I_2.3/2EtOH]I$, were prepared by the same method as above. The results suggest that the Co(II) is oxidized to Co(III) and hence they are diamagnetic in nature and their colours change on standing on air for two months.

3.1.2.3. Ligands Act in A Tridentate Manner, i.e., PTHPC and ETHTC.

In this case, we isolated two complexes with the general formulae, $[Co(C_{14}H_{15}N_4OS)I_2.H_2O]I.3H_2O$ and $[Cu(C_{14}H_{15}N_4OS)I]I.7H_2O$. The two complexes were prepared by mixing the corresponding original complexes, which were prepared by conventional chemical method, $[Co(C_{14}H_{15}N_4OS)Cl_2]Cl.2EtOH$ and $[Cu(C_{14}H_{15}N_4OS)Cl_2.H_2O]Cl.1/2EtOH$, with KI. The same procedure was used as above in order to isolate the solid complexes. The colour of the former complex was the only one which was changed on standing for a long time (two months) at room temperature (25 °C) while the other two complexes their colours remain unchanged. Also, the former and the latter complexes are diamagnetic in nature while the second one is paramagnetic in nature.

3.1.2.4. Ligands Act in Tetradentate Manner Toward Metal Ions, i.e., ATHTC and ETHTC

The last category of these types of complexes involves three complexes with the general formulae, $[Cu_2(C_8H_{18}N_4OS)I(H_2O)_3]I.H_2O$, $[Co_2(C_8H_{18}N_4OS)I_4(EtO)_2(H_2O)_2]I.1/2\ EtOH$ and $[Co_2(C_9H_{19}N_4OS).I_4]I.EtOH$. These complexes were prepared by mixing the corresponding metal complexes, $[Cu(C_8H_{18}N_4OS)Cl]½H_2O$, $[Co(C_8H_{19}N_4OS)Cl_2]1½H_2O$ and $[Co(C_9H_{19}N_4OS)Cl_2]$, in agate mortar with KI in a ratio 1:3 (complex : KI). The method of extraction for the metal complexes is the same as the other above three categories. The former complex is diamagnetic in nature while the other two complexes are paramagnetic. The colour of the former complexes is changed on standing for long time (2 months) at room temperature (25 ^{o}C) while the latter two complexes remain unchanged.

Table 6. Elemental analyses and molar conductivities of metal complexes derived from tribochemical reactions.

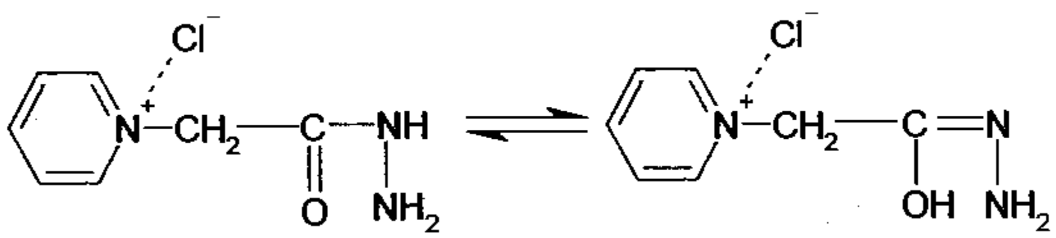
Compound	% Calcd.					% Found					Λ_m in DMF
	C	H	N	S	M	C	H	N	S	M	
$[Co(C_7H_{10}N_3O)I_2.½H_2O.½EtOH]I.H_2O$	15.0	2.5	6.6	-	9.2	14.4	2.1	6.5	-	9.0	30.8
$[Cu(C_7H_{10}N_3O)I_2][CuI_2.1/2EtOH]2H_2O$	11.4	2.0	5.0	-	15.0	10.6	0.9	4.4	-	15.0	28.4
$[Cu(C_7H_{10}N_3O)I_2][CuI_3.1/2EtOH]$	10.3	1.4	4.5	-	13.6	10.4	0.9	4.7	-	13.2	25.9
$[Cu(C_{12}H_{11}N_3OS)I.H_2O]4H_2O$	27.4	4.0	8.0	6.1	12.1	26.6	3.6	8.1	6.0	11.7	10.2
$[Co(C_{12}H_{11}N_3OS)_4.I_2]I$	40.6	3.1	11.8	9.0	4.1	41.1	2.8	11.9	9.0	4.0	34.3
$[Cu(C_{13}H_{12}N_2OS)I.H_2O]½H_2O$	33.8	3.3	6.1	6.9	13.8	33.3	2.3	6.0	6.2	13.4	10.9
$[Cu(C_{13}H_{13}N_3S)_3]I_2.1/2H_2O$	44.3	3.8	11.9	9.1	6.0	45.0	3.4	11.9	8.8	7.7	6.3
$[Cu(C_{13}H_{13}N_3S)(H_2O)I]4H_2O$	29.8	4.4	8.0	6.1	12.1	30.0	4.3	8.1	6.0	10.6	8.2
$[Co(C_{13}H_{13}N_3S)(H_2O)_4]I_3.6H_2O$	18.1	3.9	4.9	3.7	6.8	17.9	3.5	4.9	3.1	6.4	7.9
$[Co(C_9H_{19}N_4OS)I_3.½EtOH]I$	14.6	2.7	6.8	3.9	7.2	14.6	2.4	7.6	3.6	6.6	24.7
$[Co_2(C_9H_{19}N_4OS)I_4]I.EtOH$	12.8	2.4	5.4	3.1	11.4	12.2	1.8	5.3	2.9	11.0	35.5
$[Co(C_8H_{18}N_4OS)I_2.3/2EtOH]I$	18.2	3.7	7.7	4.4	8.1	17.7	3.8	7.2	4.2	7.6	31.6
$[Co(C_{14}H_{15}N_4OS)I_2.H_2O]I.3H_2O$	21.0	2.9	7.0	4.0	7.4	20.6	2.5	6.9	3.8	7.4	38.6
$[Cu(C_{14}H_{15}N_4OS)I]I.7H_2O$	23.0	4.0	7.7	4.4	8.7	22.6	3.3	7.6	3.9	9.0	29.7
$[Cu_2(C_8H_{18}N_4OS)I(H_2O)_3]I.H_2O$	14.3	3.9	8.3	4.8	18.9	14.1	3.5	8.1	3.8	18.6	26.4
$[Co_2(C_8H_{18}N_4OS)I_4(EtO)_2(H_2O)_2]I.1/2EtOH$	13.9	3.2	5.0	2.9	10.5	13.7	3.1	5.0	2.7	10.7	30.1

3.2. Infrared and ^{1}H-NMR Spectra of the Free Ligands

A substantial part of knowledge concerning the active centers, the most important functional groups as well as the presence or absence of hydrogen bonding within the free ligands can be achieved by applying spectroscopic techniques (UV, IR, ^{1}H-NMR, Mass). An insight in the type of bond exists and the positions of the groups in space can also be gained by a careful examination of the IR spectra of organic compounds in solid, liquid and/or organic solvents (polar and/or non-polar). The purpose of our studies herein is to relate the structures of the free ligands with its metal complexes which will be discussed in details hereafter. Also, one of our goals her is to determine the active centers through which the coordination process to the metal ion is carried out. Moreover, the spectral will provided us with the stereochemistry of both the ligands and its metal complexes. Finally, the spectra (intra – or inter-) exist in solid state or in solution.

3.2.1. Spectral Studies (IR, ^{1}H-NMR) of [1-(Carboxymethyl) Pyridinium Chloride Hydrazide] (G.P.).

G.P exists in two tautomeric forms ,i.e., keto form (structure 1a) and enol form (structure 1b).



(structure 1a, keto form) (structure 1b, enol form)

The infrared spectrum of G.P in KBr (Fig. 1) shows three strong bands at 3459, 3343 and 3220 cm^{-1} assigned to $\upsilon_{as}(NH_2)$, $\upsilon_s(NH_2)$ and $\upsilon(NH)$ vibrations, respectively. Also, the two strong bands observed at 1693 and 1635 cm^{-1} are assigned to $\upsilon(CO)$ and $\beta(NH_2)$ vibrations, respectively. The observation of all these bands as sharp and strong bands lends support that G.P is mainly existed in the keto form (structure 1). Moreover, the spectrum shows two strong bands at 1540 and 1004 cm^{-1} assignable to amide II[(29)] and υ(N-N)[(30)] vibrations, respectively. The weak broad bands observed in the 2700 – 1900 cm^{-1} region are assigned to the quaternary ammonium salt (pyridinium chloride)[(31)].

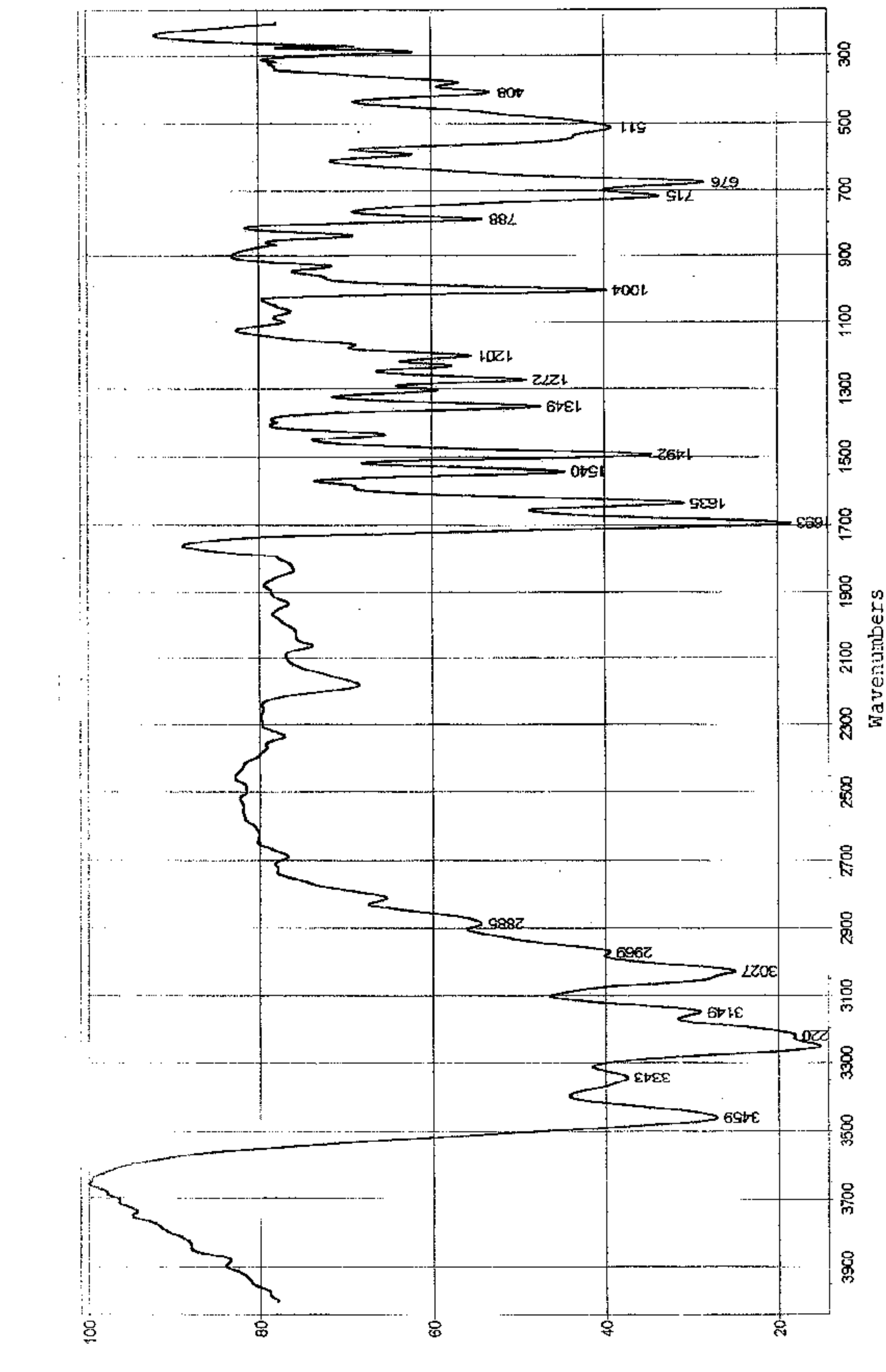
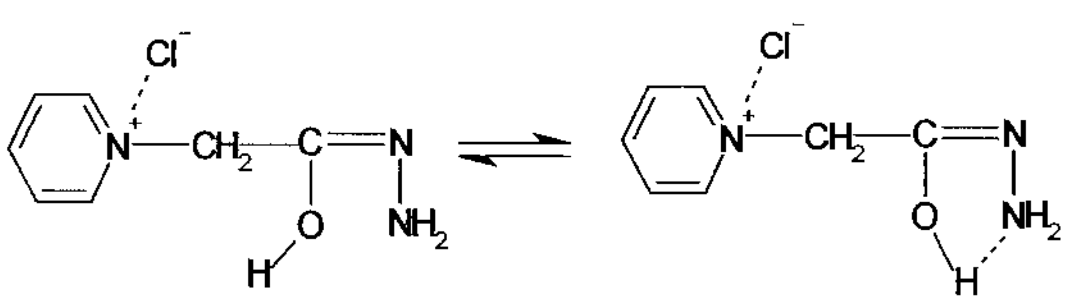


Fig. 1. Infrared spectrum of Girard's P (G.P.) in KBr.

The ^{1}H-NMR spectrum of G.P in d_6-DMSO (Figs.2,3) shows a strong singlet signal at 5.45 p.p.m. as well as a broad single signal at 4.46 p.p.m., downfield with respect to TMS, assignable to the protons of CH_2 and NH_2, respectively. The multiple signals in the 9.03–8.18 p.p.m. are assigned to the protons of the pyridine group. Moreover, three sharp signals are observed at 9.21, 5.74 and 4.65 p.p.m., downfield with respect of TMS, assignable to the protons of the enolized OH (hydrogen-bonded), OH (free) and NH, respectively. The observation of all these signals suggests that G.P exists as a mixture of keto and enol forms in d_6-DMSO (structures 1 and 2). Also, the results suggest that the enol form is existed in two forms, i.e., free enolized OH (structure 2a) and hydrogen-bond enolized OH (structure 2b).



(structure 2a) (structure 2b)

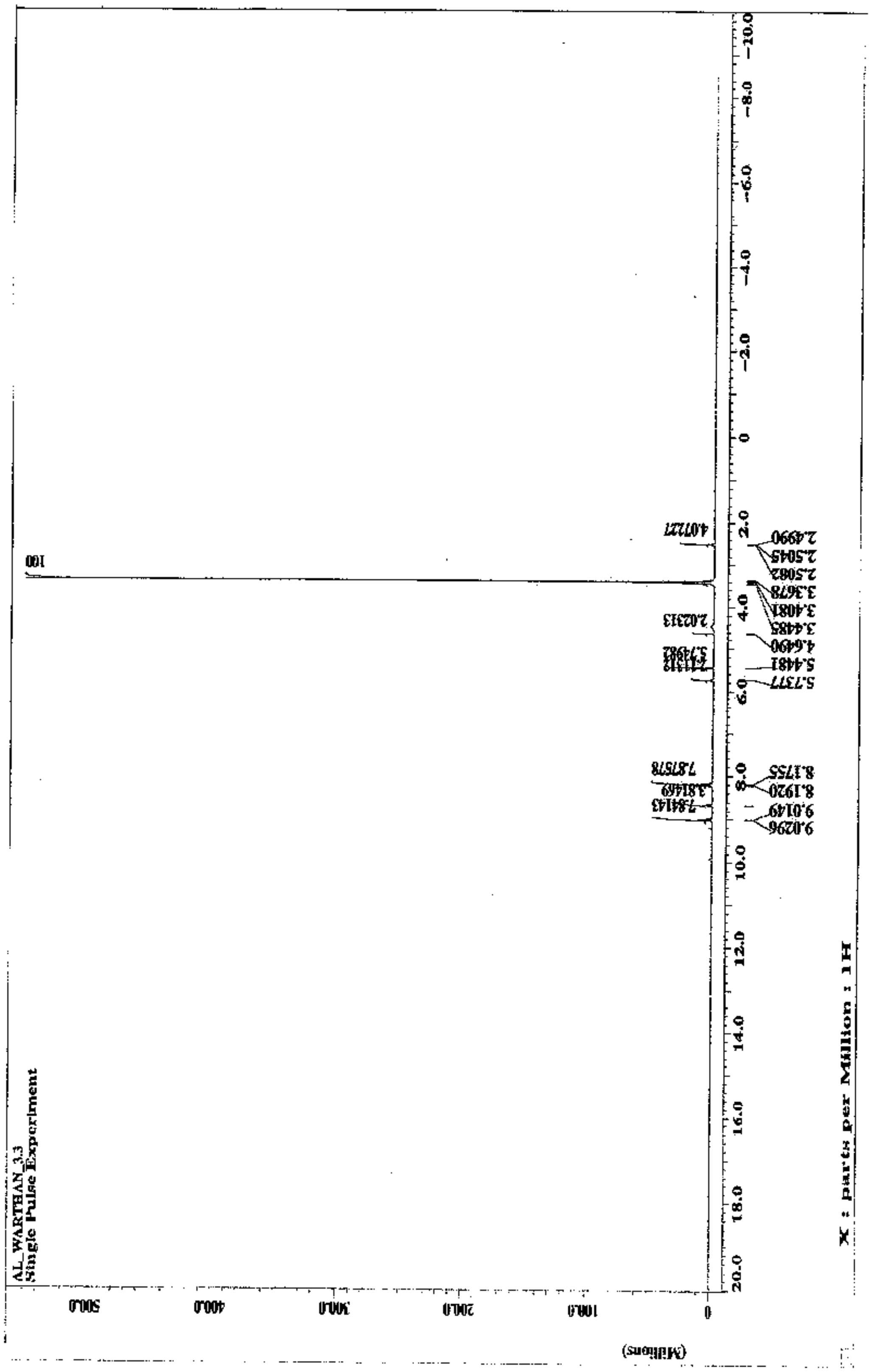


Fig. 2. ^{1}H-NMR spectrum of Girard's P (G.P.) in d_6-DMSO.

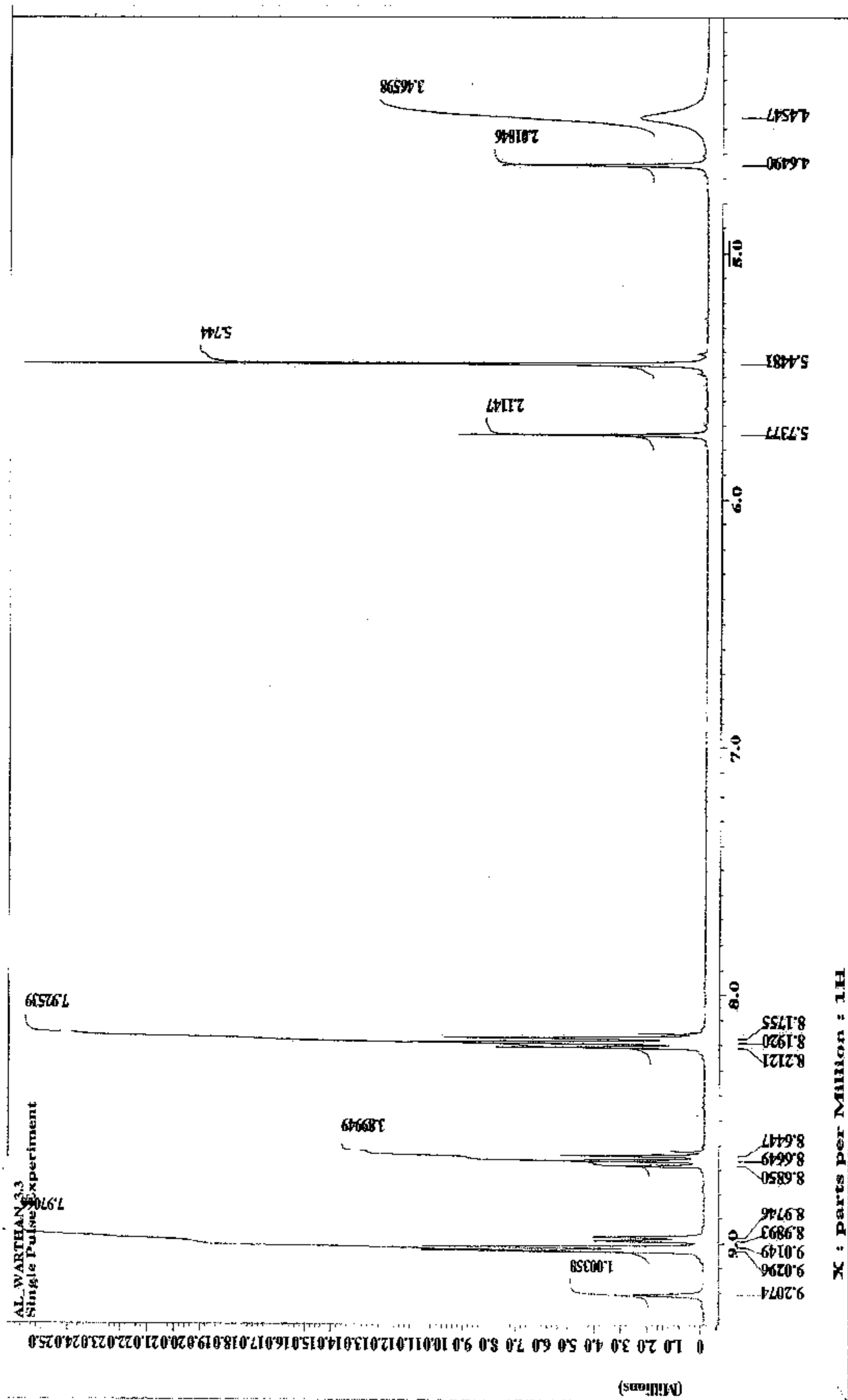
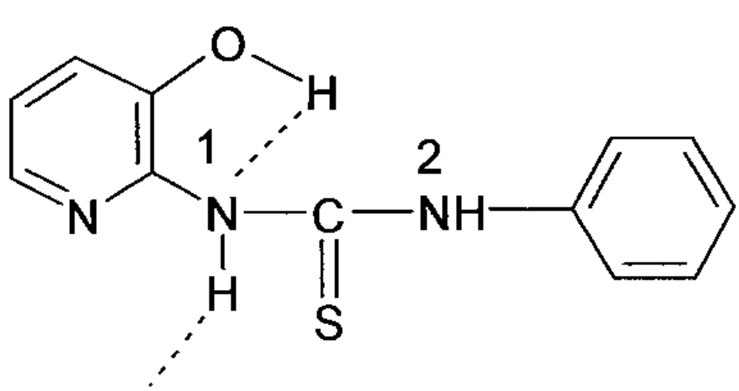


Fig. 3. ^{1}H-NMR spectrum of Girard's P (G.P.) in d_6-DMSO .

All these foundations suggest that G.P is mainly existed in the keto form in the solids state as shown from IR spectra while it exists as a mixture of keto and enol in d_6-DMSO as shown from ^{1}H-NMR data.

3.2.2. Spectral Studies (IR, ^{1}H-NMR) of N-(3-Hydroxypyridine 2-yl)–N'–Phenylthiourea (HPPTU).

The IR spectrum of HPPTU in KBr (Fig. 4) shows a medium broad band centered at 3434 cm^{-1} together with a shoulder at 3520 cm^{-1} assignable to υ(^{2}NH) and υ(OH) vibrations, respectively. Another shoulder is observed at 3380 cm^{-1} assignable to is assigned to υ(^{1}NH) vibration. The existence of those two shoulders at 3434 and 3380 cm^{-1} suggests that both those two groups participate in hydrogen bonding as shown in structure 3. The band observed at 1646 cm^{-1} is assigned to υ(C=N) (pyridine) vibration.



(structure 3)

The bands observed at 1548, 1502 and 1456 cm^{-1} in the HPPTU spectrum may be due to υ(-N-C=S)[32,33] vibrations. These bands are assigned as coupled modes consist principally of β(NH) and υ(CN). Also, the bands at 1257 and 748 cm^{-1} are due to υ(C=S) with a contribution of υ(CN)[34]. The broad weak bands observed in the 1800-2000 and 2500-2200 cm^{-1} regions suggest the presence of intra-molecular hydrogen bonding of the type O-H....N[35]. ^{1}H-NMR spectrum of HPPTU in d_6-DMSO (Fig. 5) shows three singlet signals with equal intensity (1:1:1) at 10.96, 8.24 and 7.86 p.p.m., downfield with respect to TMS, assignable to the protons of OH, ^{1}NH and ^{2}NH, respectively. Multiple protons in the 7.01–8.22 p.p.m. region are commensurate with eight protons of the pyridyl and phenyl groups.

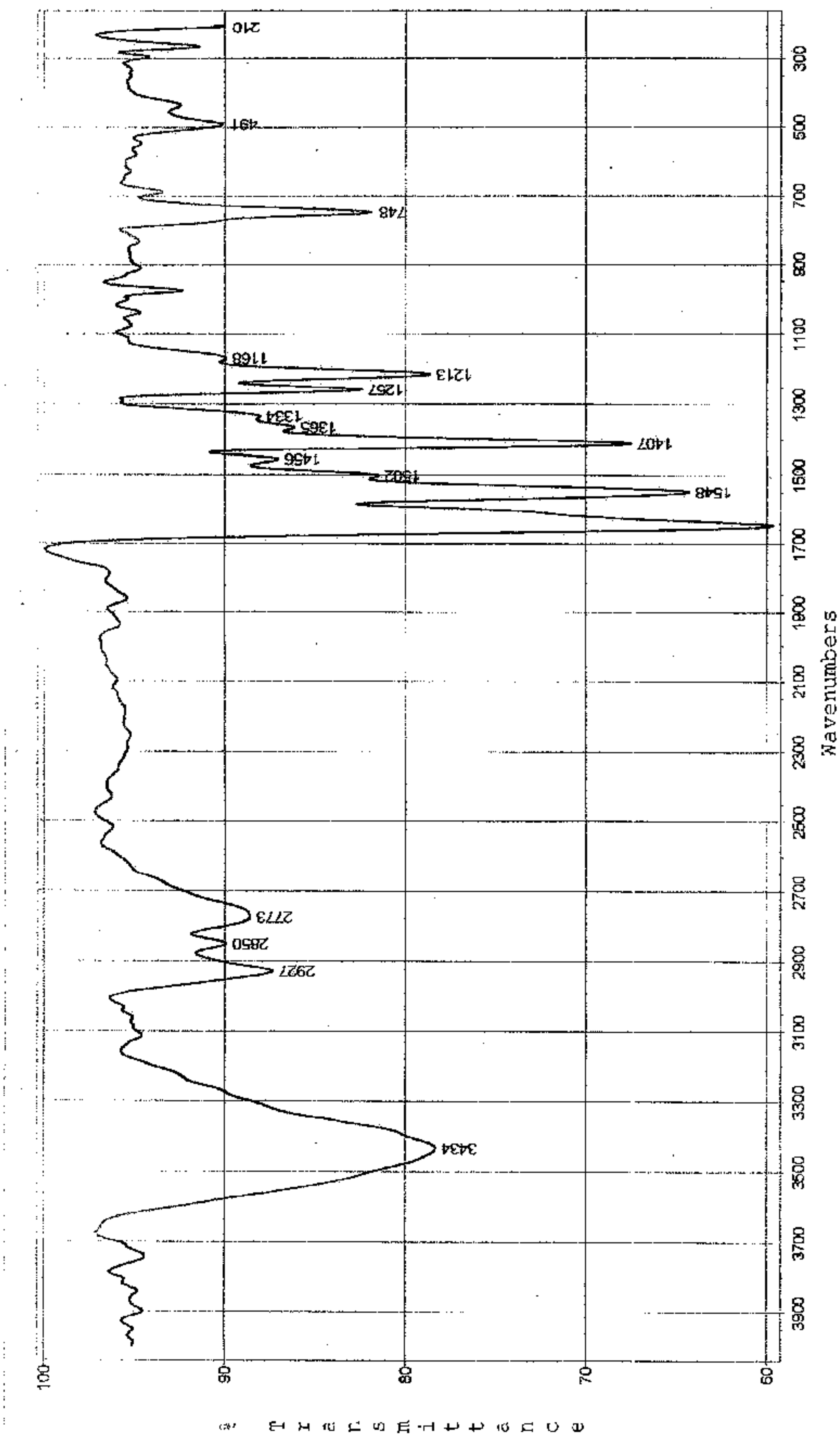


Fig. 4. Infrared spectrum of N-(3-hydroxypyridine – 2-y1)-N'- phenylthiourea (HPPTU) in KBr.

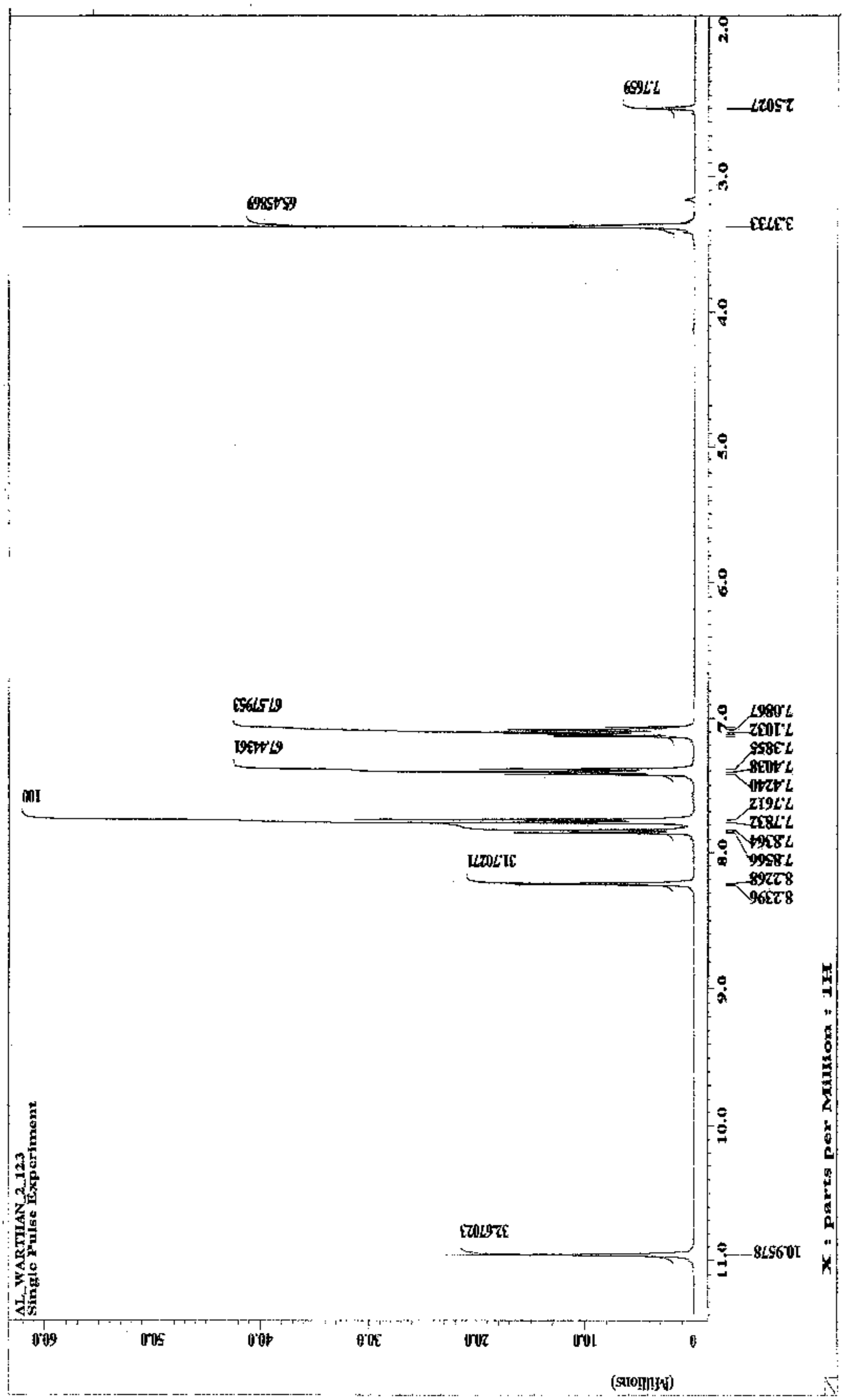
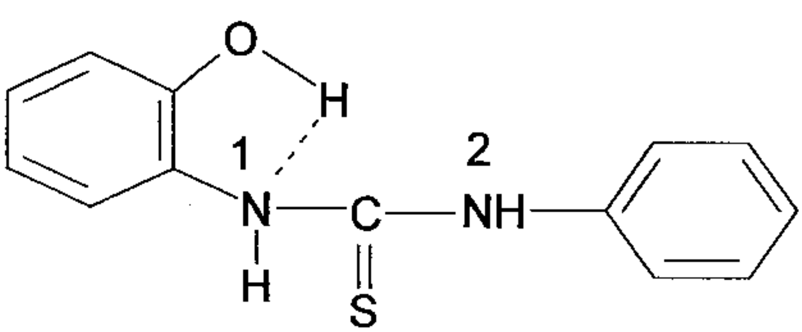


Fig. 5. [1]H-NMR spectrum of N-(3-hydroxypyridinium -2y1) –N'-phenylthiourea (HPPTU) in d_6–DMSO.

3.2.3. Spectral Studies (IR, ^{1}H-NMR) of N-2-(3-Hydroxypyridyl) –N'-Phenylthiourea (3-HPPTU).

The IR spectrum of 3–HPPTU in KBr (Fig. 6) shows two strong bands at 3820 and 3156 cm^{-1} assigned to υ(^{1}NH) vibrations[32], respectively. The weak band observed at 3520 cm^{-1} is assigned to υ(OH) vibration. The weakness of this band supports our view that this group is probably involved in hydrogen bonding. Also, the observation of weak broad bands in the 2100-1900 and 2500-2300 cm^{-1} regions suggests the presence of intra-molecular hydrogen bonding of the type O-H.....N[35] as shown in structure 4. On comparing the IR spectra of 3-HPPTU (Fig. 5) with HPPTU (Fig. 6), we observed that the band at 1646 cm^{-1} (Fig. 5) assigned to υ (C=N) (pyridine) is obscured in Fig. 6. This is mainly due to the replacement of the pyridine moiety by phenyl group.



(structure 4)

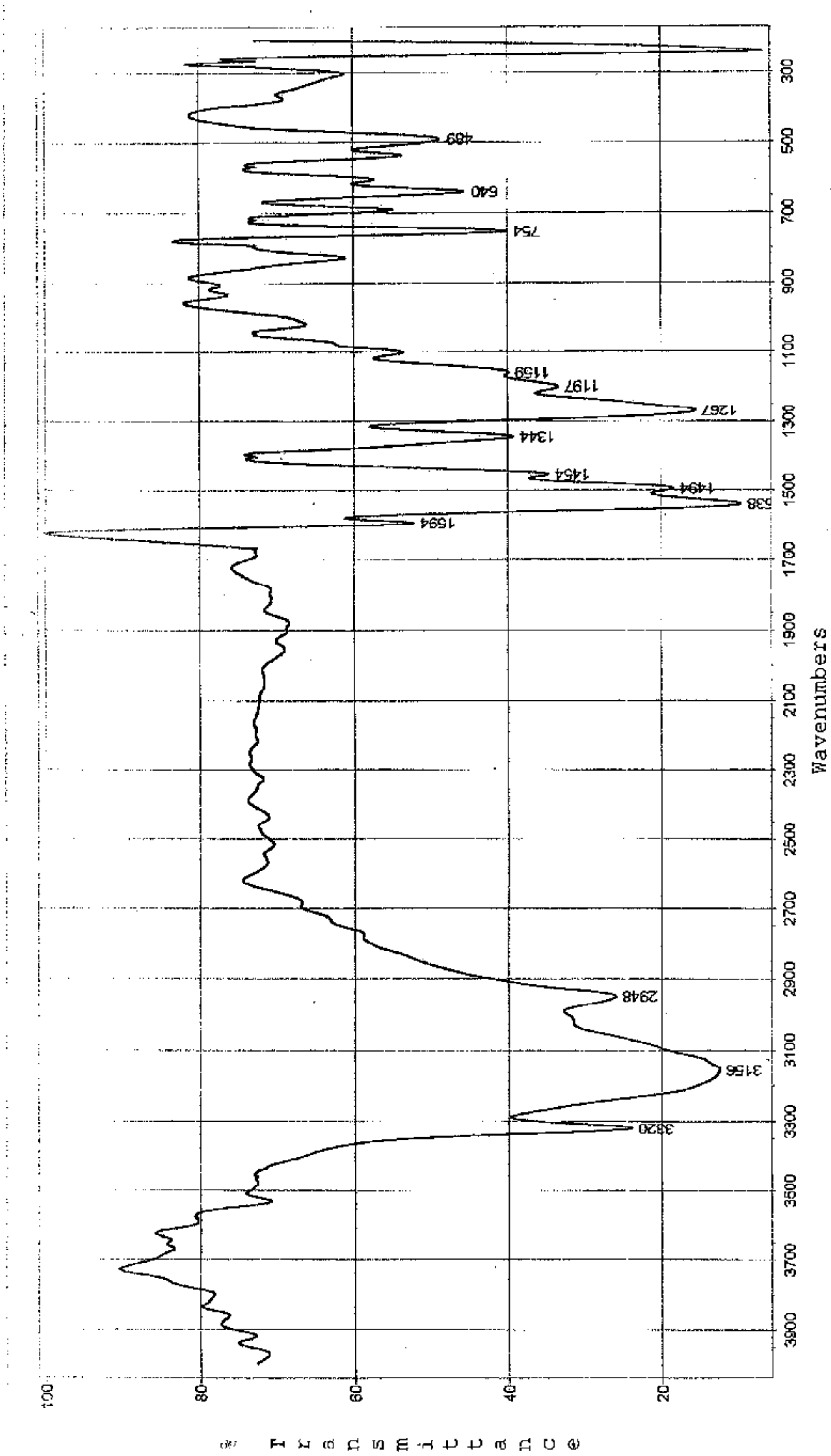


Fig. 6. Infrared spectrum of N-2- (3-hydroxyphenyl) -N'-phenylthiourea (3-HPPTU) in KBr.

The bands observed at 1538, 1494 and 1454 cm^{-1} may be due to υ(-N-C=S)[32,33,36] vibrations, respectively. These bands are assigned as coupled modes consist principally of β(NH). Also, the bands at 1267 cm^{-1} and 754 cm^{-1} are due to υ(C=S) with a contribution of υ(CN)[34]. The band observed at 1594 cm^{-1} is mainly due to υ(C=C) (phenyl).

The ^{1}H–NMR spectrum of 3-HPPTU in d_6-DMSO (Fig. 7) shows two singlet signals at 9.98 and 9.87 p.p.m. with equal intensity (1:1), downfield with respect to TMS, assignable to the protons of OH (hydrogen-bonded) and OH (free). Also, the two singlet signals at 9.12 and 8.10 p.p.m are assigned to the protons of ^{1}NH and ^{2}NH, respectively. Multiple protons in the 6.79 - 7.58 region are commensurate with nine protons of the two phenyl groups.

3.2.4. Spectral Studies (IR, ^{1}H-NMR) of N-2-(3-Methyl-Pyridine) – N' – Phenylthiourea (3-MPTU).

The IR spectrum of 3-HPPTU in KBr (Fig. 8) shows a strong band at 3397 cm^{-1}, together with a weak band at 3087 cm^{-1} assigned to υ NH(2) and υ NH(1) vibrations, respectively. Two bands at 1255 and 742 cm^{-1} are attributed to υ(CS) vibrations and four bands at 1631, 1592, 1570 and 1511 cm^{-1} are assigned to υ(C=N) and υ(C=C) vibrations of the pyridyl and phenyl groups[37]. All the above bands are observed at 3208, 3170, 1598, 1553, 1498, 1250 and 741 cm^{-1} in N-2-pyridyl-N'–phenylthiourea[38].

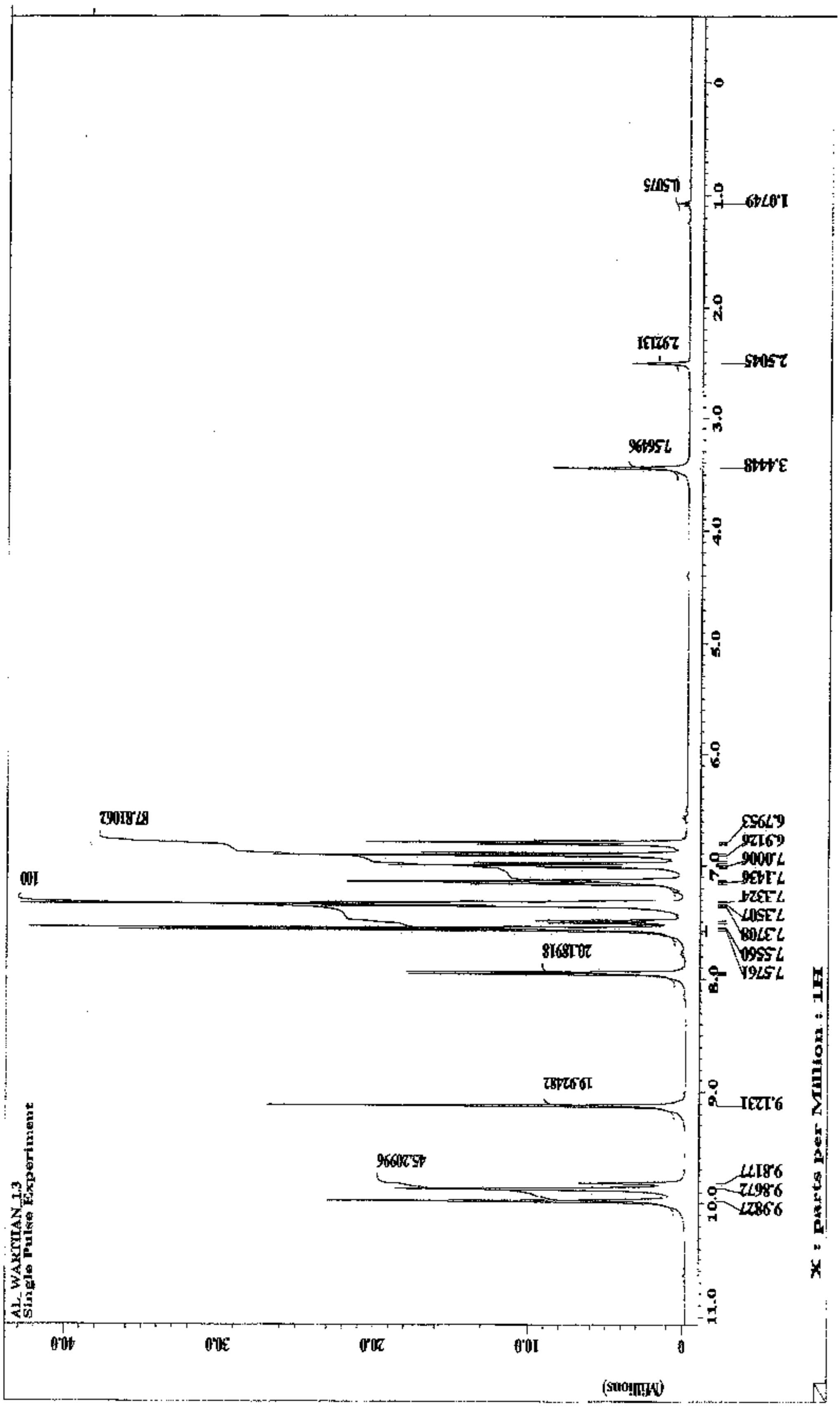


Fig.7. ^{1}H-NMR spectrum of N-2- (3-hydroxyphenyl)-N'-phenylthiourea (3-HPPTU) in d_6 –DMSO.

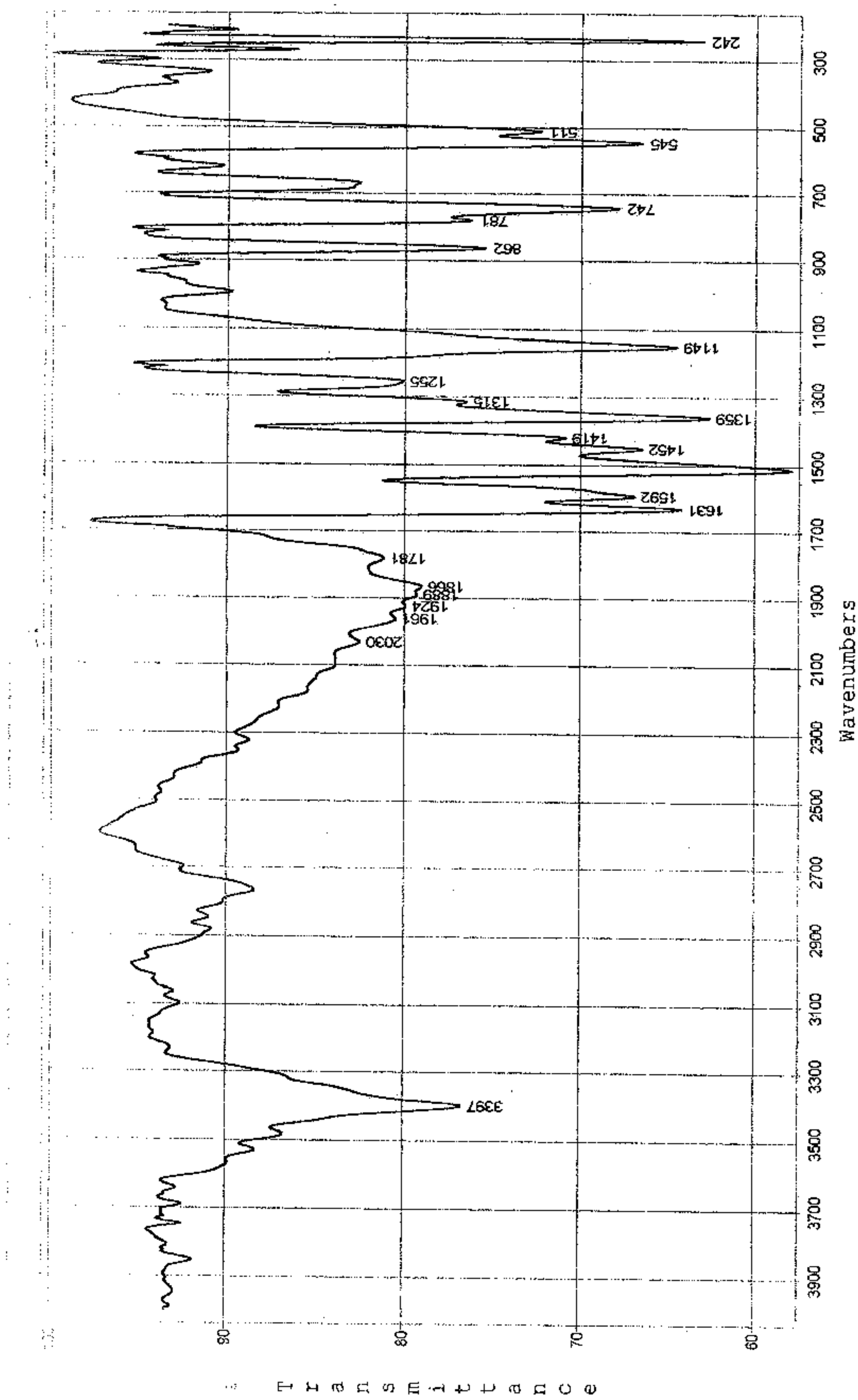
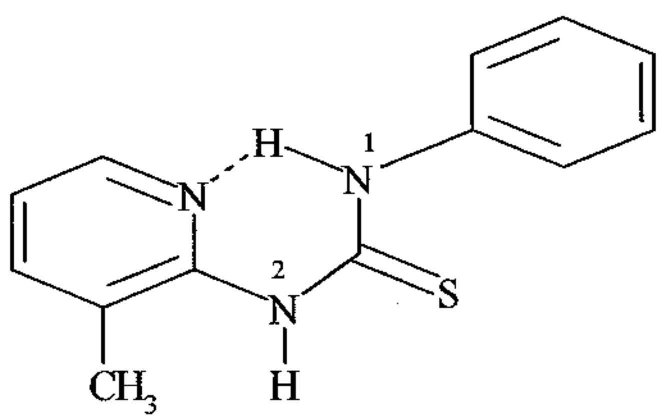


Fig. 8 . Infrared spectrum of N-2-(3-methylpyridine) –N'-phenylthiourea (3-MPTU) in KBr.

The electron–donating group (CH_3) attached to the pyridyl ring in position-3 probably leads to a decrease in the conjugation of the lone pair on the NH (2) group.

Hence, the NH(2) band appears at higher wavenumbers in comparison to that observed in the spectrum of N-2- pyridyl–N′-phenylthiourea (HPYPT). Also, the observation of NH(1) as a weak band (3087 cm^{-1}) at lower wavenumber to HPPYT, suggests that this group is strongly influenced by hydrogen bonding. The hydrogen bonding probably occurs between the pyridyl nitrogen and NH(1) forming a six-member ring as shown in structure 5.



(structure 5)

Moreover, the υ(C=C) and υ(C=N) pyridyl ring vibrations are shifted to higher wavenumbers in 3-MPTU compared to HPYPT. This behaviour is mainly due to the effect of hydrogen bonding as well as to the presence of methyl group. Finally, the observation of bands due to the thioketo group at 1255 and 742 cm^{-1} in

HPYPT and 3–MPTU suggests that this group is not taking part in hydrogen bonding and is not affected by the methyl group[39].

The ^{1}H-NMR spectrum of 3-MPTU in d_6-DMSO (Fig. 9) shows singlet signals at 13.7, 9.1 and 2.4 p.p.m., downfield with respect to TMS, attributable to the N(1), N(2) and CH_3 protons, respectively. The absence of any proton signal due to the SH group is taken as evidence that 3-MPTU exists mainly in the thioketo form. Multiple signals in the 7.0-8.2 p.p.m. region are commensurate with eight protons and are assigned to the protons of the pyridyl and phenyl groups.

3.2.5. Spectral Studies (IR, ^{1}H-NMR) of N-2-(6-Methylpyridyl) –N'-Phenylthiourea (6-MPTU).

The IR spectrum of 6-MPTU (Fig. 10) is similar to a great extent to that of 3-MPTU (Fig.5). On comparison of both spectra, we observed that the positions of all bands are quite similar except few of which are differ in their intensities and positions. The bands at 3396 and 3070 cm^{-1} are assigned to υ NH(2) and υ NH(1) vibrations, respectively. Also, the two bands at 1251 and 742 cm^{-1} are attributed to υ(CS) vibration.

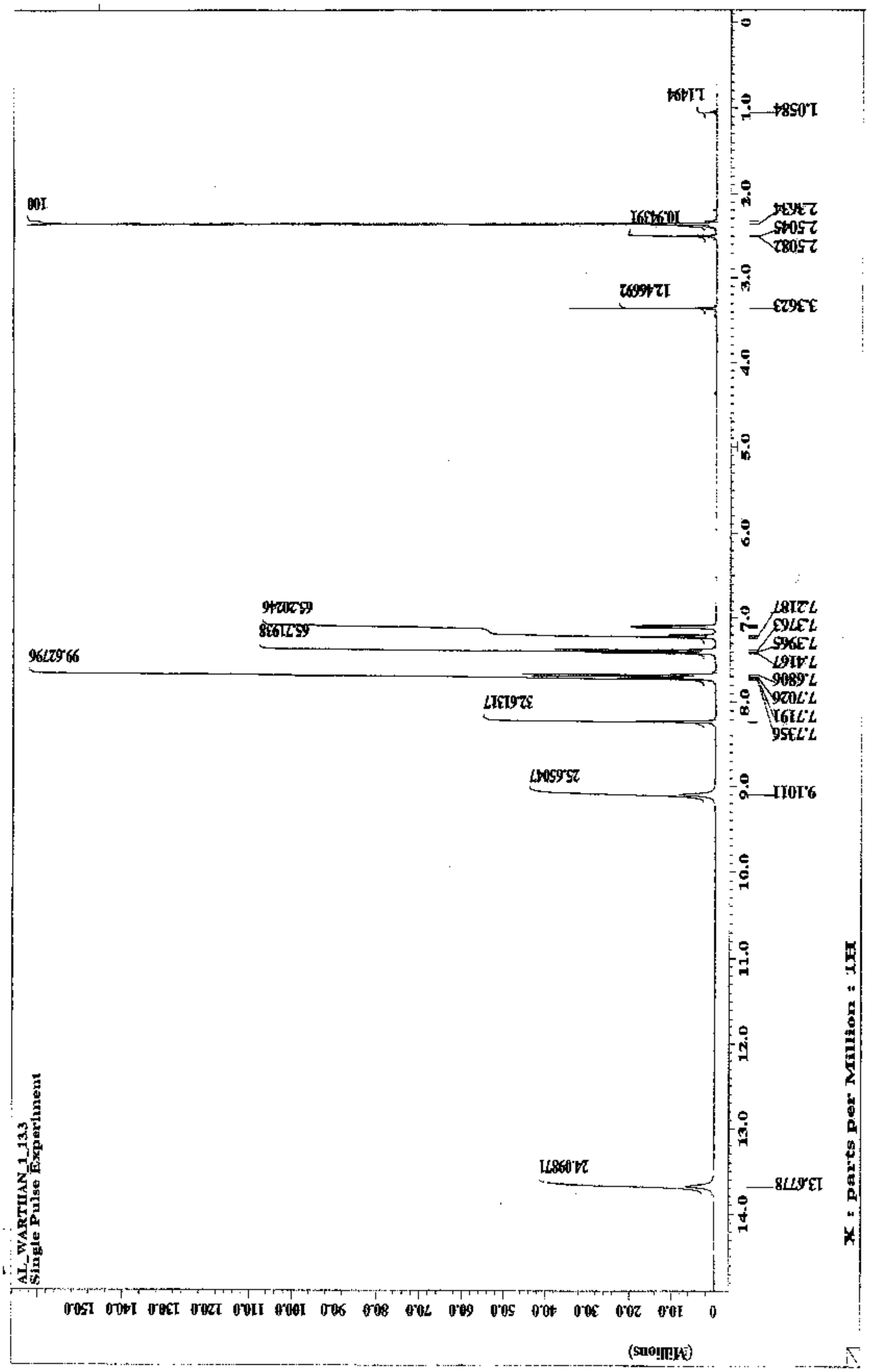


Fig. 9. ^{1}H-NMR spectrum of N-2- (3-methylpyridine) –N'-phenylthiourea (3-MPTU) in d_6 – DMSO.

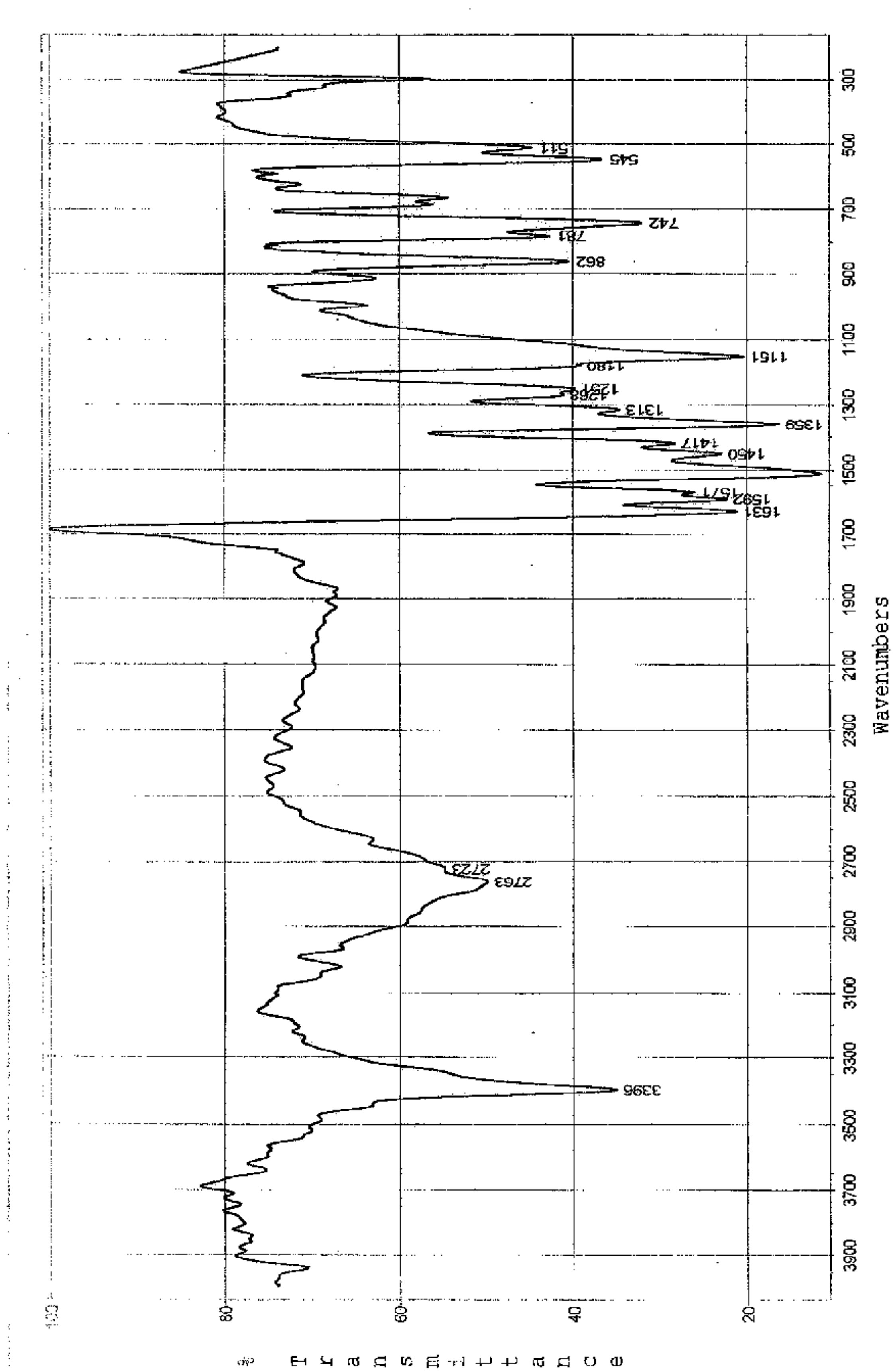
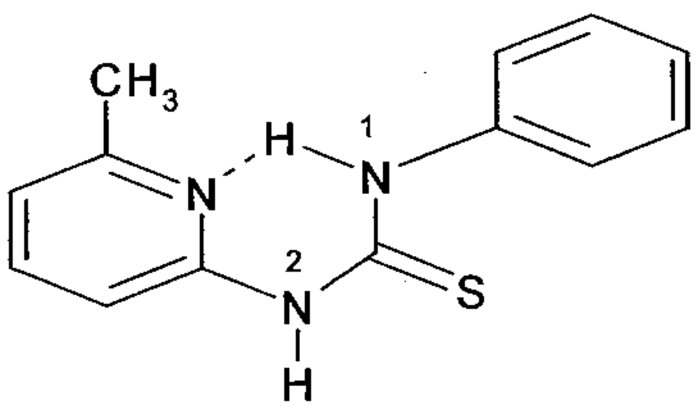


Fig. 10. Infrared spectrum of N-2- (6-methylpyridine) –N'-phenylthiourea (6-MPTU) in KBr.

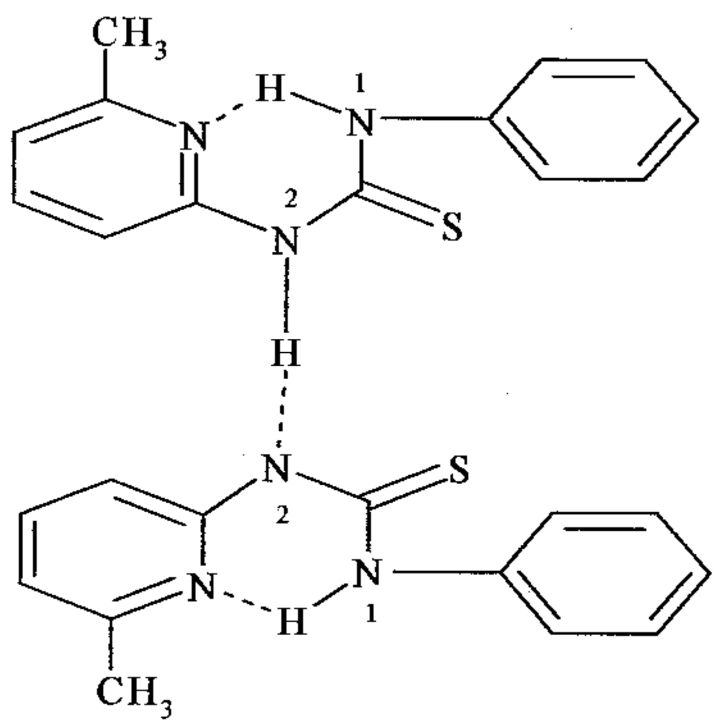
Moreover, the four bands at 1631, 1592, 1571 and 1511 cm^{-1} are assigned to υ(C=N) and υ(C=C) vibrations of the pyridyl and phenyl groups[37], respectively. All the above bands are observed at 3397, 3087, 1255, 742, 1631, 1592, 1572 and 1511 cm^{-1} in the spectrum of 3-MPTU. The observation of NH(1) as a weak band (3070 cm^{-1}) at lower wavenumber comparing to 3-MPTU, suggests that this group is more influenced by hydrogen bonding than in case of 6-MPTU. The hydrogen bonding probably occurs between the pyridyl nitrogen and NH(1) forming a six-member ring as shown in structure 6.



(structure 6)

The electron donating group (CH_3) attached to the pyridyl ring in position-6 probably leads to increase the electron density on the pyridyl nitrogen and hence the hydrogen bond of the type N....H – ^{1}N will be more stronger than in case of 3-MPTU. The shift of the NH (1) to lower wavenumber proves to some extent the strength of this bond.

The ^{1}H-NMR spectra of 6-MPTU (Figs.11-13) in d_6- DMSO show singlet signals at 14.2, 13.68, 10.85, 9.1 and 3.40 p.p.m., downfield with respect to TMS. The first two singlets are attributed to NH(1) (intra-molecular hydrogen bonded) and NH(1) (free) while the third and fourth singlets (10.85, 9.01 p.p.m.) may be attributed to NH(2) (inter-molecular hydrogen-bonded) and NH(2) (free). The latter singlet at 3.4 p.p.m. is attributed to the protons of CH_3 group. The observation of two singlets for NH(2) suggests that this group may be contribute in inter- molecular hydrogen bonding as shown in structure 7.



(structure 7)

On comparison the position of the CH_3 group in case of 6-MPTU (3.40 p.p.m.) with that of 3-MPTU (2.36 p.p.m.), we observed that the position of this group in the former case is shifted upfield. This may be due to the effect of the presence of the methyl group near to the pyridyl nitrogen causing the shift of this band.

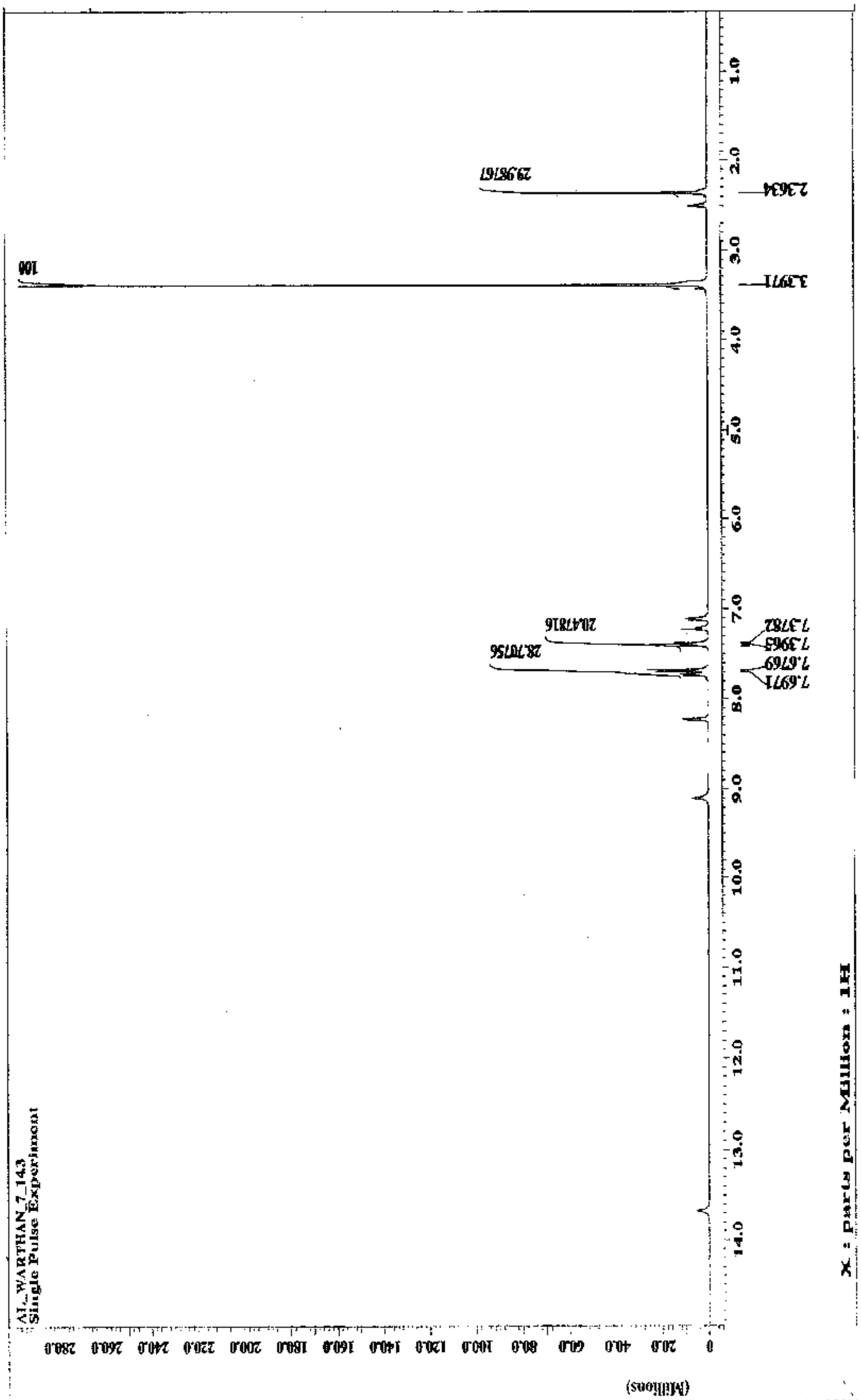


Fig. 11. ^{1}H-NMR spectrum of N-2- (6-methylpyridine) –N'- phenylthiourea (6-MPTU) in d_6-DMSO.

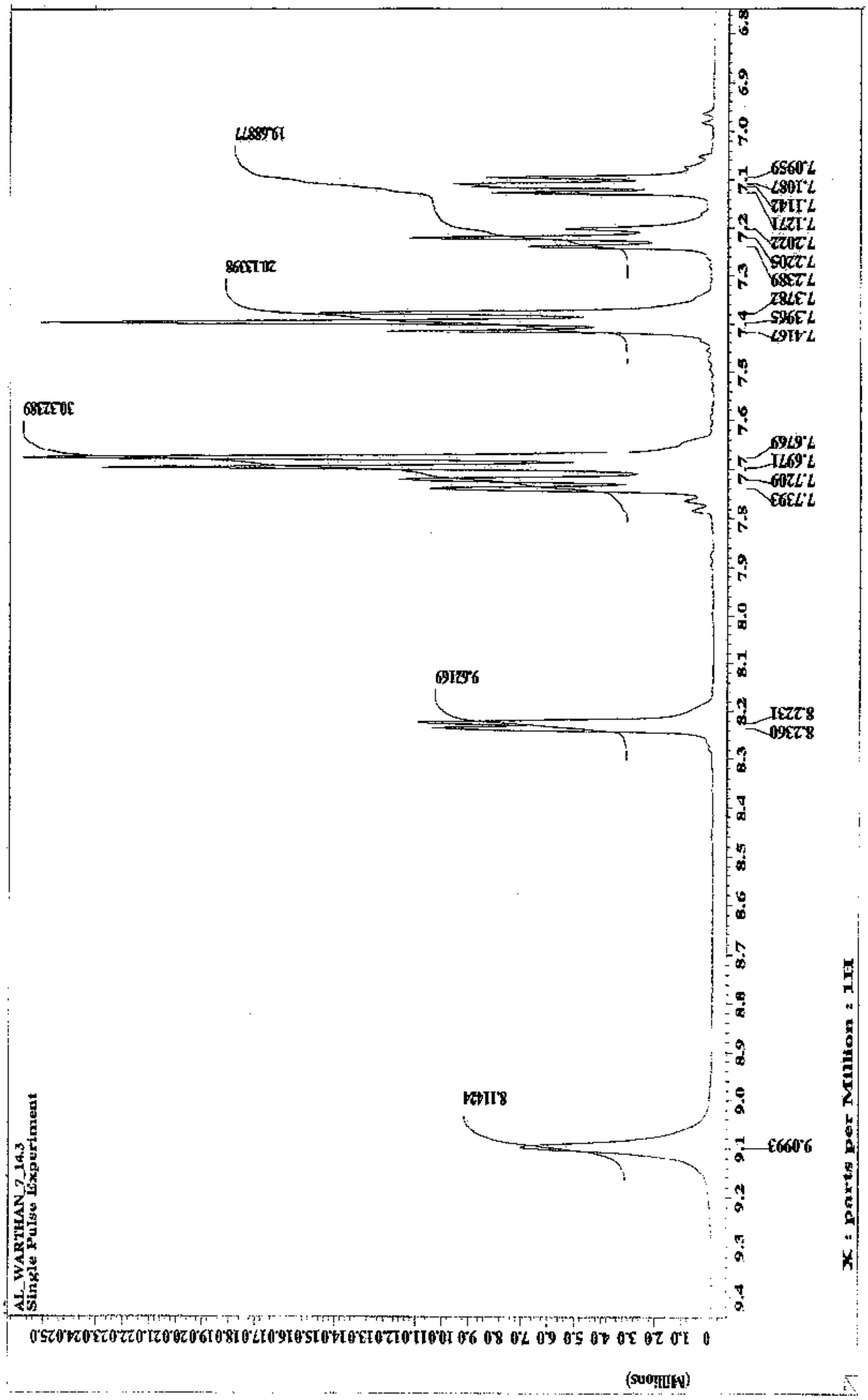


Fig. 12. ^{1}H-NMR spectrum of N-2-(6-methylpyridine)-N'- phenylthiourea (6-MPTU) in d_6-DMSO.

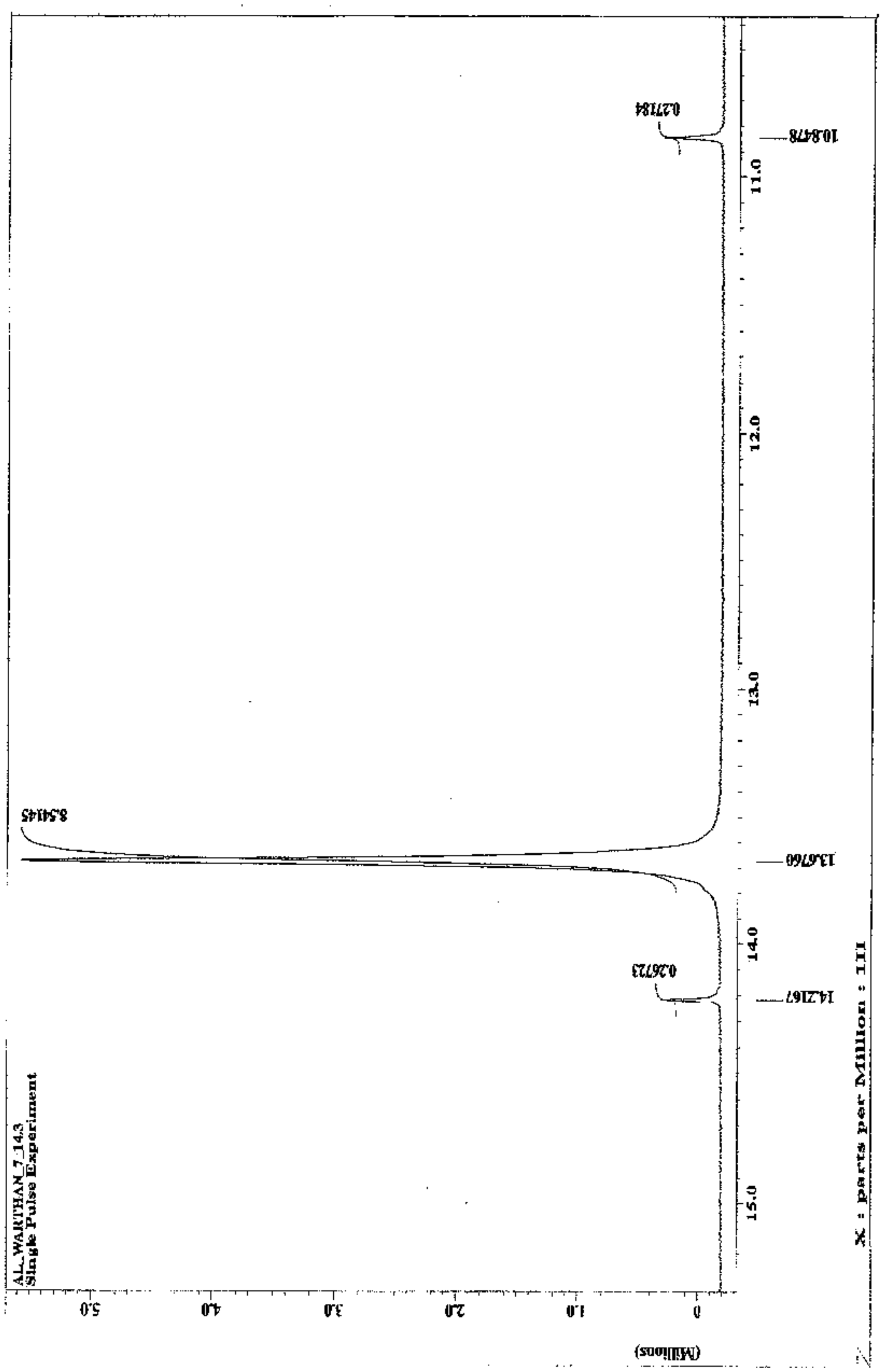
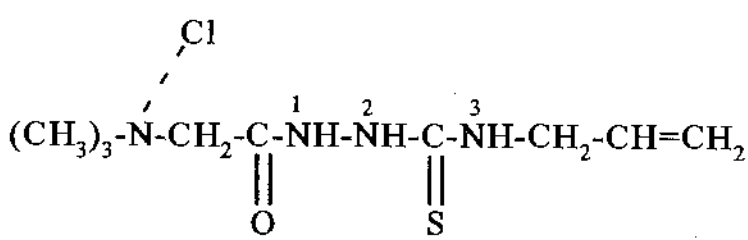


Fig. 13. ^{1}H-NMR spectrum of N-2- (6-methylpyridine)-N'-phenylthiourea (6-MPTU) in d_6-DMSO.

3.2.6. Spectral Studies (IR, ^{1}H-NMR) of N-{[(allylamino) thioxomethyl] hydrazinocarbonyl methy1} trimethyl ammonium chloride (ATHTC).

The infrared spectrum of ATHTC in KBr (Fig.14) indicates that the ligand (ATHTC) exists mainly in the keto form. The spectrum shows υ(CO) and υ(CS) vibration bands at 1700 and 1222 cm^{-1}, respectively, and no bands above 3480 cm^{-1} as well as in the region 2600-2550 cm^{-1} which be expected for the eno1 forms are observed. The three bands at 1544, 1471 and 1415 cm^{-1} in the spectrum of ATHTC are likely due to υ(-N-C=S)[33,40] vibrations. These bands are assigned as coupled modes principally of β(NH) and υ(CN)[34]. The three bands at 3210, 3164 and 3100 cm^{-1} are assigned to υNH(1), υNH(2) and υNH(4) vibrations, respectively. Also, the band at 916 cm^{-1} is assigned to υ(N-N) vibration[30]. All these foundations suggest structure (8) for ATHTC.



(structure 8)

The ^{1}H–NMR spectra of ATHTC in d_6-DMSO (Figs. 16,17) show two singlet signals at 10.87 and 4.43 p.p.m., downfield with respect to TMS, assigned to NH(1) and NH(2), respectively. The signal assigned to NH(4) appears as a triplet signal centered at 8.54 p.p.m. Also, the two singlet signals with ratio 3:2 at 3.26 and 3.43 are assigned to the protons of CH_3 and CH_2(N.CH_2), respectively. Moreover, the spectra (Figs. 15 and 16) show a sextet signal centered at 5.80 p.p.m. assigned to the proton of CH.

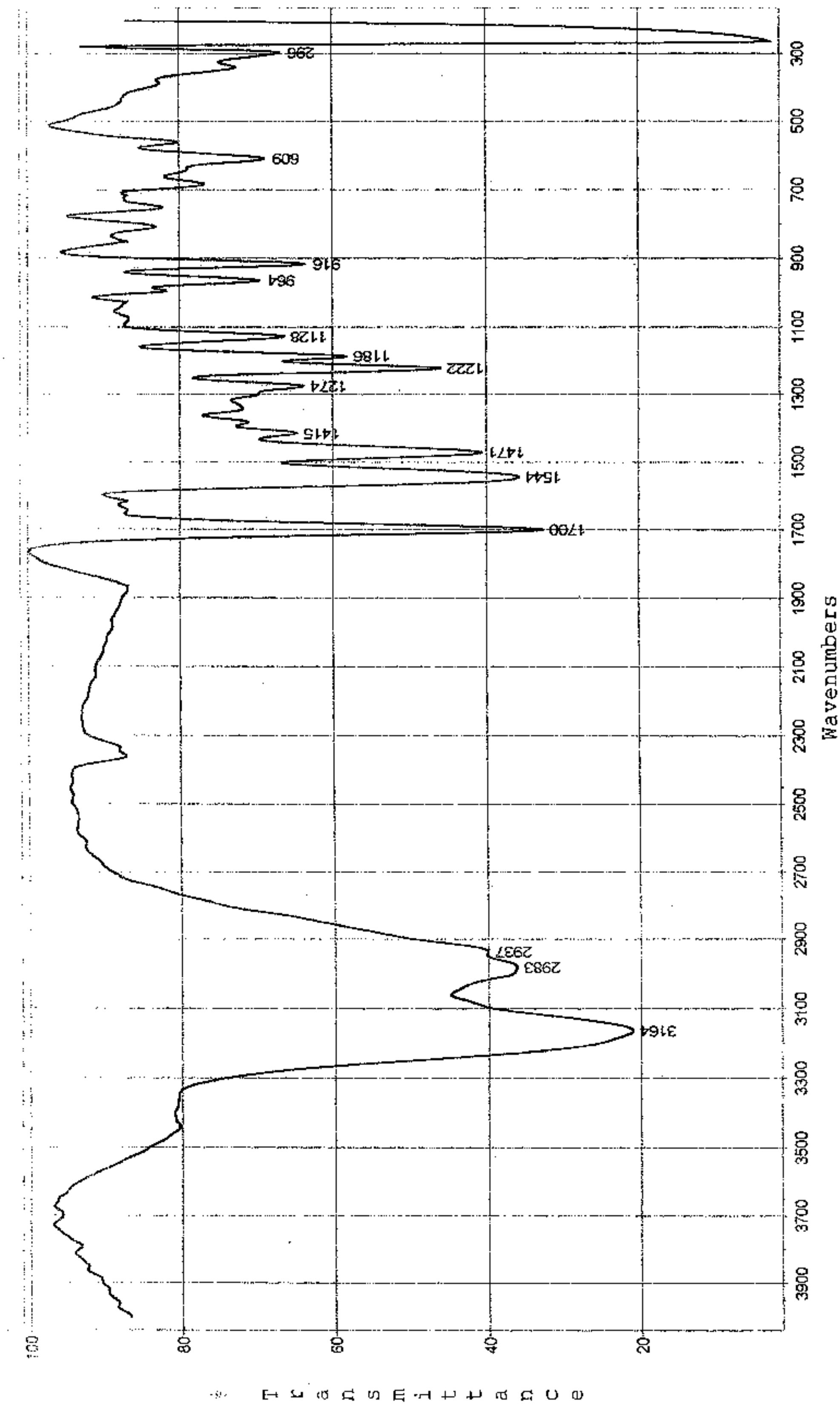


Fig. 14. Infrared spectrum of N- {[(allylamino) thioxomethyl] hydrazinocarbonyl methyl} trimethylammonium chloride (ATHTC) in KBr.

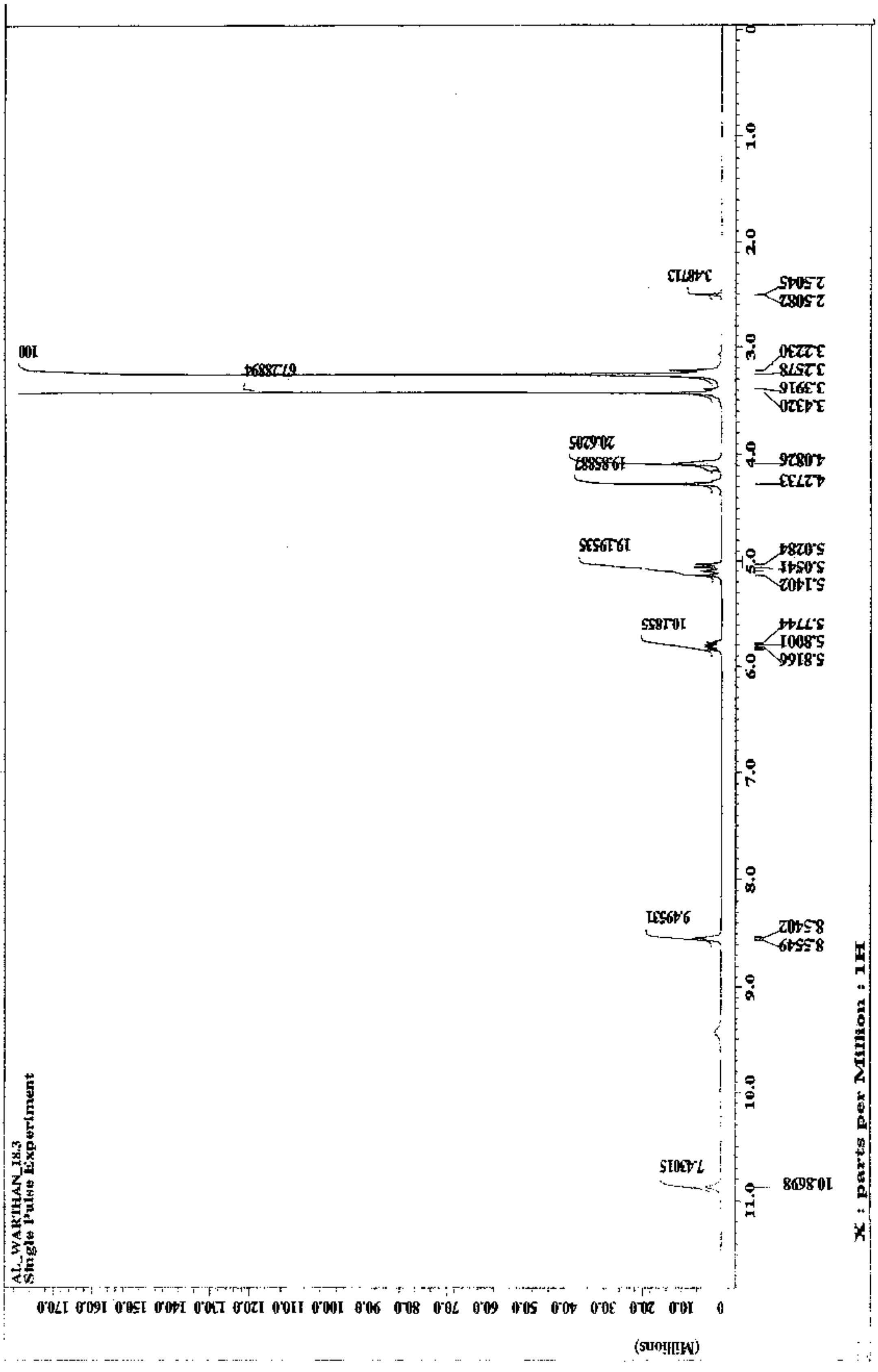


Fig. 15. **^{1}H-NMR spectrum of N-{[(allylamino) thioxomethyl] hydrazinocarbonyl methyl} trimethyl ammonium chloride (ATHTC) in d_6- DMSO.**

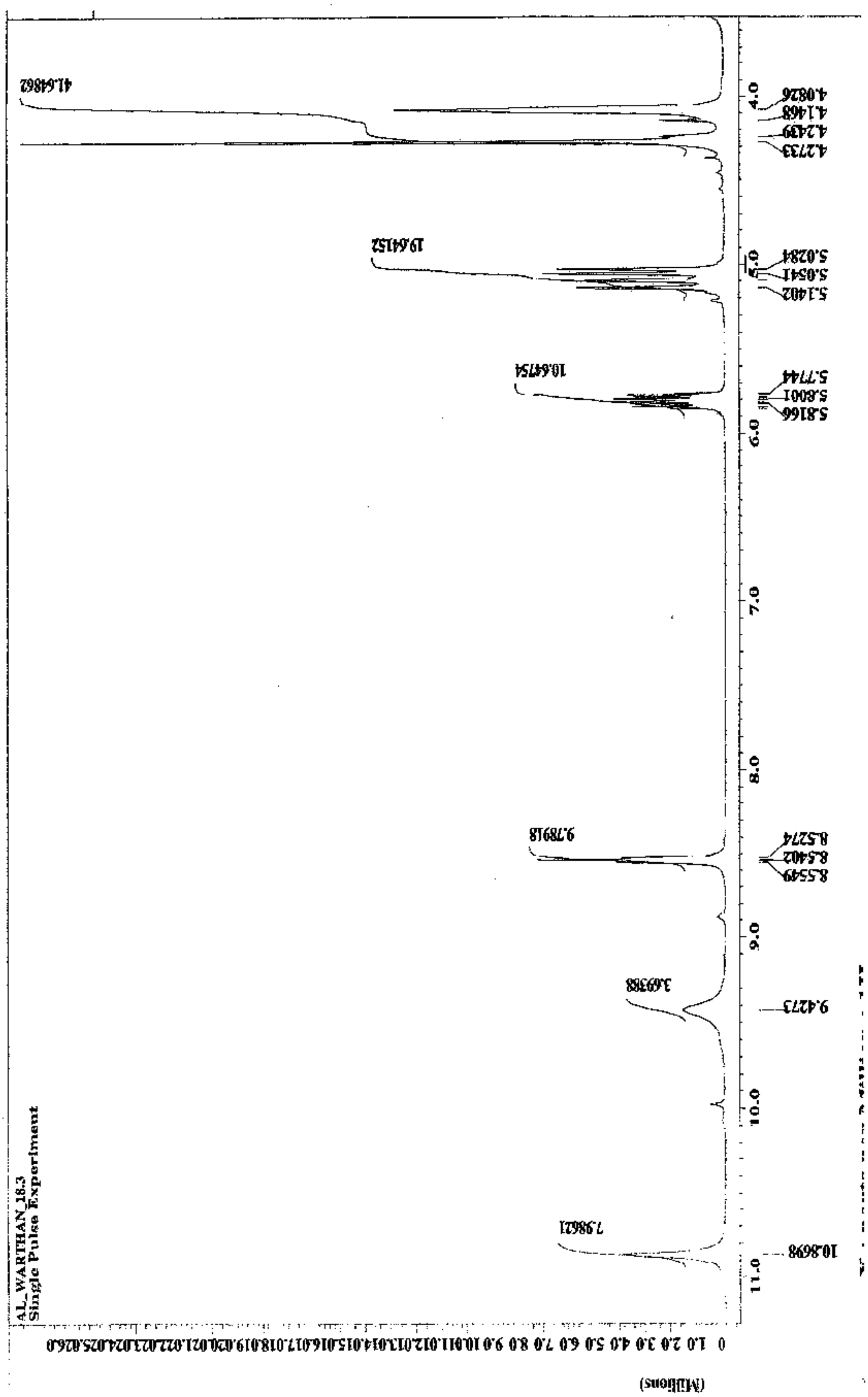


Fig. 16. ^{1}H-NMR spectrum of N-{[(allylamino) thioxomethyl] hydrazinocarbonyl methyl} trimethylammonium chloride (ATHTC) in d_6-DMSO.

Finally, the quartet signal at 5.05 and the doublet signal at 4.27 p.p.m. are assigned to the protons of CH_2(-NH-CH_2) and CH_2(-CH=CH_2), respectively.

3.2.7. Spectral Studies (IR, ^{1}H-NMR) of {[(Ethylamino) Thioxomethyl] Hydrazinocarbonyl Trimethylammonium Chloride (ETHTC).

The IR spectrum of ETHTC in KBr (Fig.17) shows three bands at 3320, 3139 and 3090 cm^{-1} assigned to υ NH(1), υNH(2) and υNH(4), respectively. Also, the bands at 1550, 1484 and 1450 cm^{-1} are assigned to υ(-N-C=S)[32,33] vibrations. These bands are attributed as coupled modes consist principally of β(NH) and υ(CN) vibrations, respectively. Moreover, the bands at 1290 and 740 cm^{-1} are due to υ(C=S) with a contribution of υ(CN)[34]. The carbonyl oxygen band (CO) is observed as a strong band at 1704 cm^{-1}. The absence of any bands due to OH or SH suggests that the ligand is mainly existed in the keto form. All these foundations suggest structure (9) for ETHTC.

$$(CH_3)_3\text{-}\overset{\cdot\cdot Cl}{N}\text{-}CH_2\text{-}CO\text{-}\overset{1}{N}H\text{-}\overset{2}{N}H\text{-}CS\text{-}\overset{4}{N}H\text{-}CH_2\text{-}CH_3$$

(structure 9)

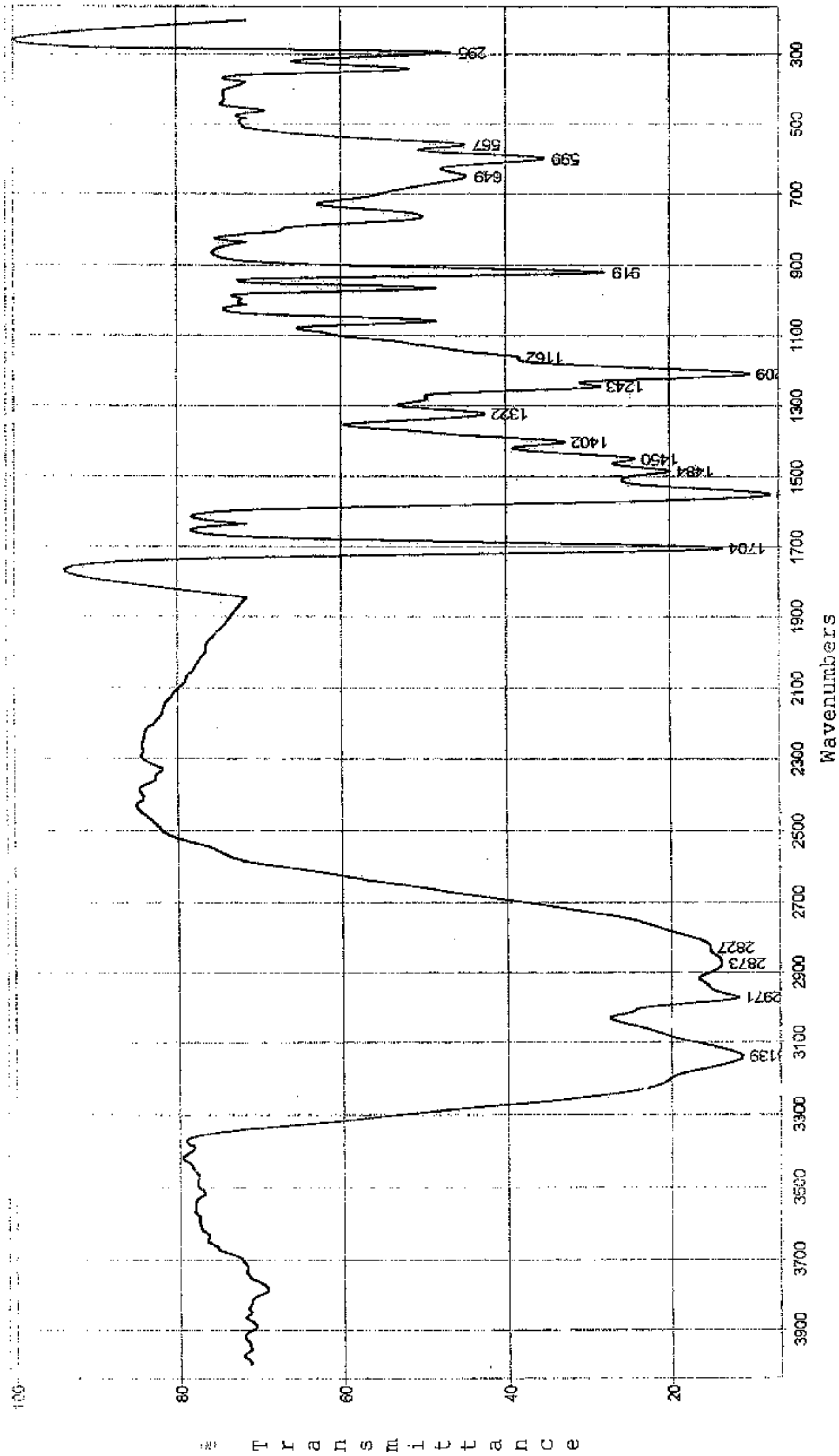


Fig. 17. IR spectrum of N-{[(ethylamino) thioxometyl] hydrazioncarbonyl} trimethylammonium chloride (ETHTC) in KBr.

The ^{1}H-NMR spectra of ETHTC in d_6-DMSO (Figs.18 and 19) show three singlet signals at 10.76, 9.35 and 7.51 p.p.m., downfield with respect to TMS, assigned to the protons of NH(1), NH(2) and NH(4), respectively,

A triplet signal centered at 1.06 p.p.m. is attributed to the methyl of the ethyl group ($-CH_2-CH_3$), while the CH_2 group of the ethyl group is observed as a quintet signal centered at 3.44 p.p.m. Meanwhile, the trimethyl groups [$\{CH_3)_3$] of G.T exists as a singlet signal at 3.25 p.p.m. Finally, the CH_2 of the ($-CH_2-$CO) group is observed as a singlet signal at 4.28 p.p.m.

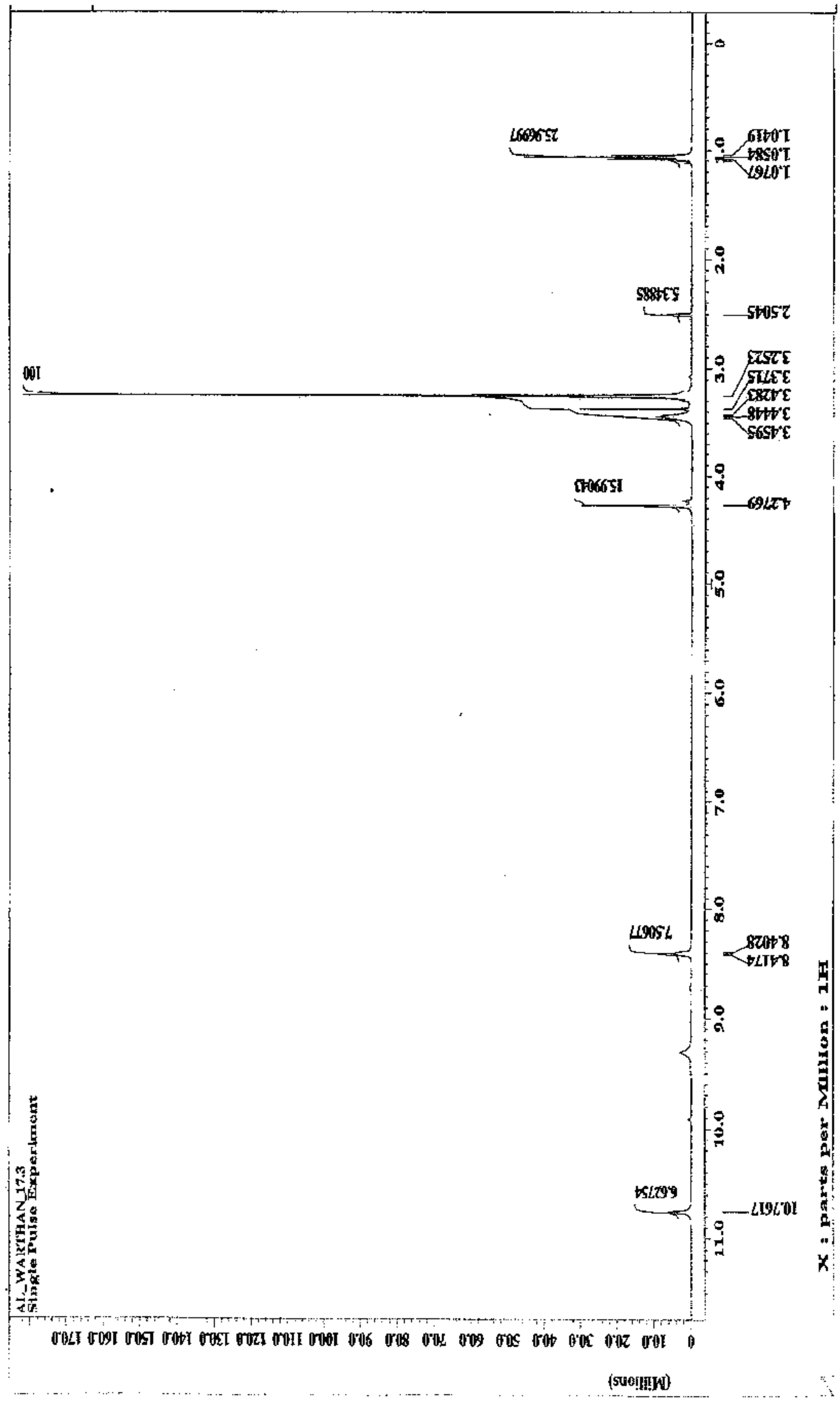


Fig. 18. ^{1}H-NMR spectrum of N-{[(ethylamino) thioxomethyl] hydrazinocarbonyl} trimethylammonium chloride (ETHTC) in d_6-DMSO.

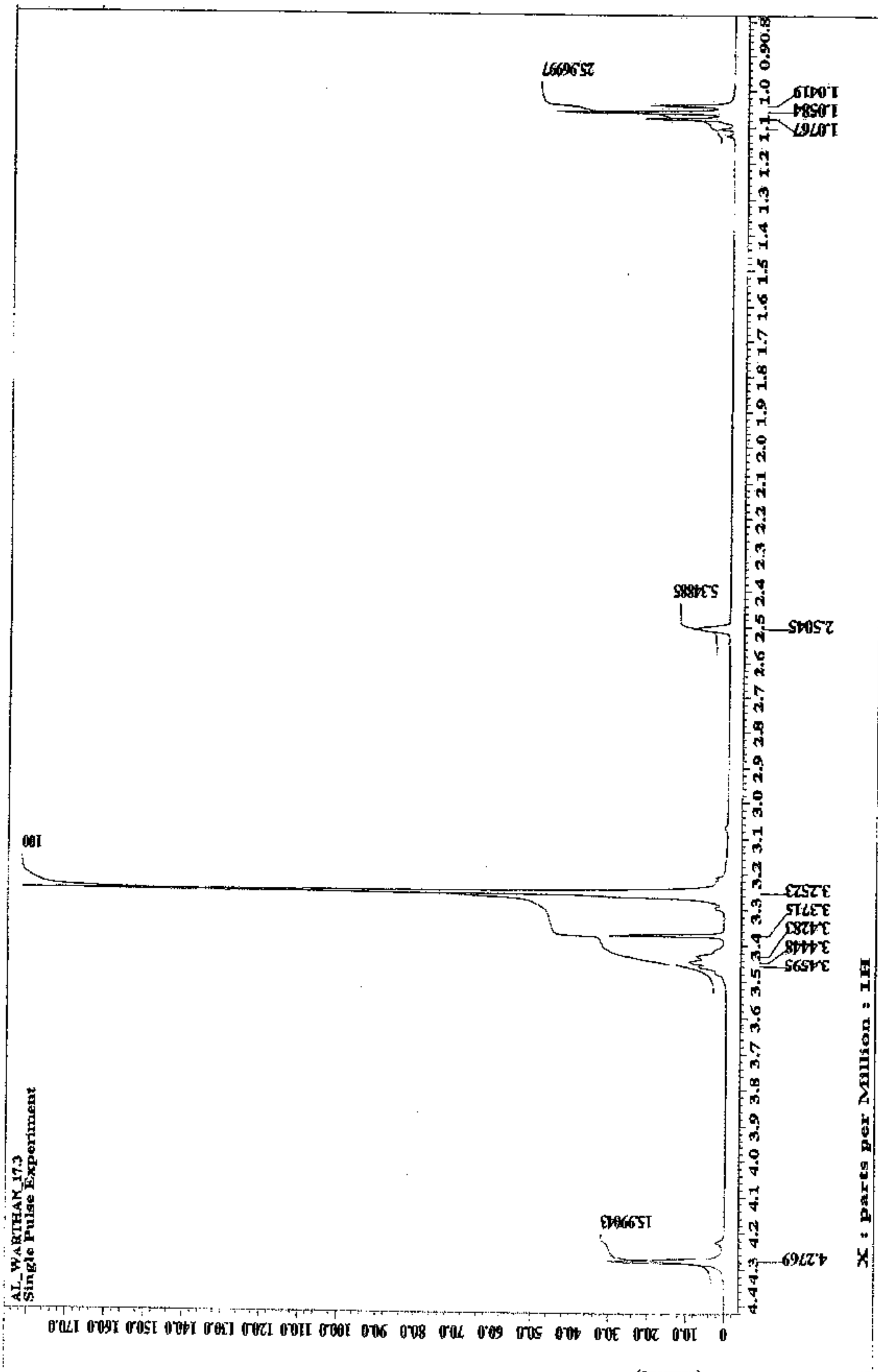
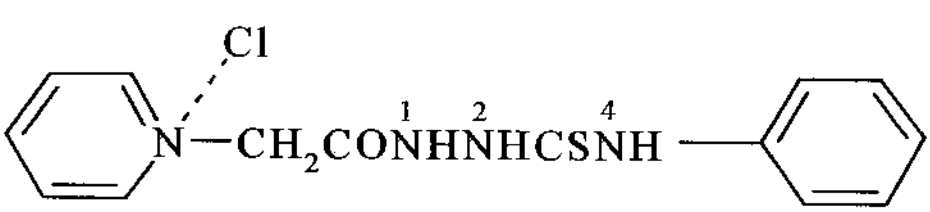


Fig. 19. ^{1}H-NMR spectrum of N-{[(ethylamino) thioxomethyl] hydrazinocarbonyl} trimethylammonium chloride (ETHC) in d_6-DMSO.

3.2.8. Spectral Studies (IR, ^{1}H-NMR) of N-{[Phenylamino Thioxomethyl] Hydrazinocarbonylmethy]} Pyridinium Chloride (PTHPC).

Three sharp bands at 3286, 3210 and 3021 cm^{-1} in the IR spectrum of PTHPC (Fig.20) are observed and assignable to υNH(1), υNH(2) and υNH(4) vibrations, respectively. The four bands at 1635, 1595, 1533 and 1492 cm^{-1} are assigned to υ(C=N) and υ(C=C) vibrations of the pyridyl and the phenyl groups(37). Also, the two bands at 1197 and 746 cm^{-1} are attributed to υ(CS) vibration. The strong sharp band at 1700 cm^{-1} is assigned to the carbonyl oxygen group. The absence of any bands in the 1900–2200 and 2300-2500 cm^{-1} regions due to hydrogen bonding supports that PTHPC exists in the keto form. Also, the obscure of any band in the 2600–2550 cm^{-1} region due to υ(SH) band indicates that the ligand exists in the thioketo form rather than the thioenol form. The results suggest structure (10) for PTHPC.



(structure 10)

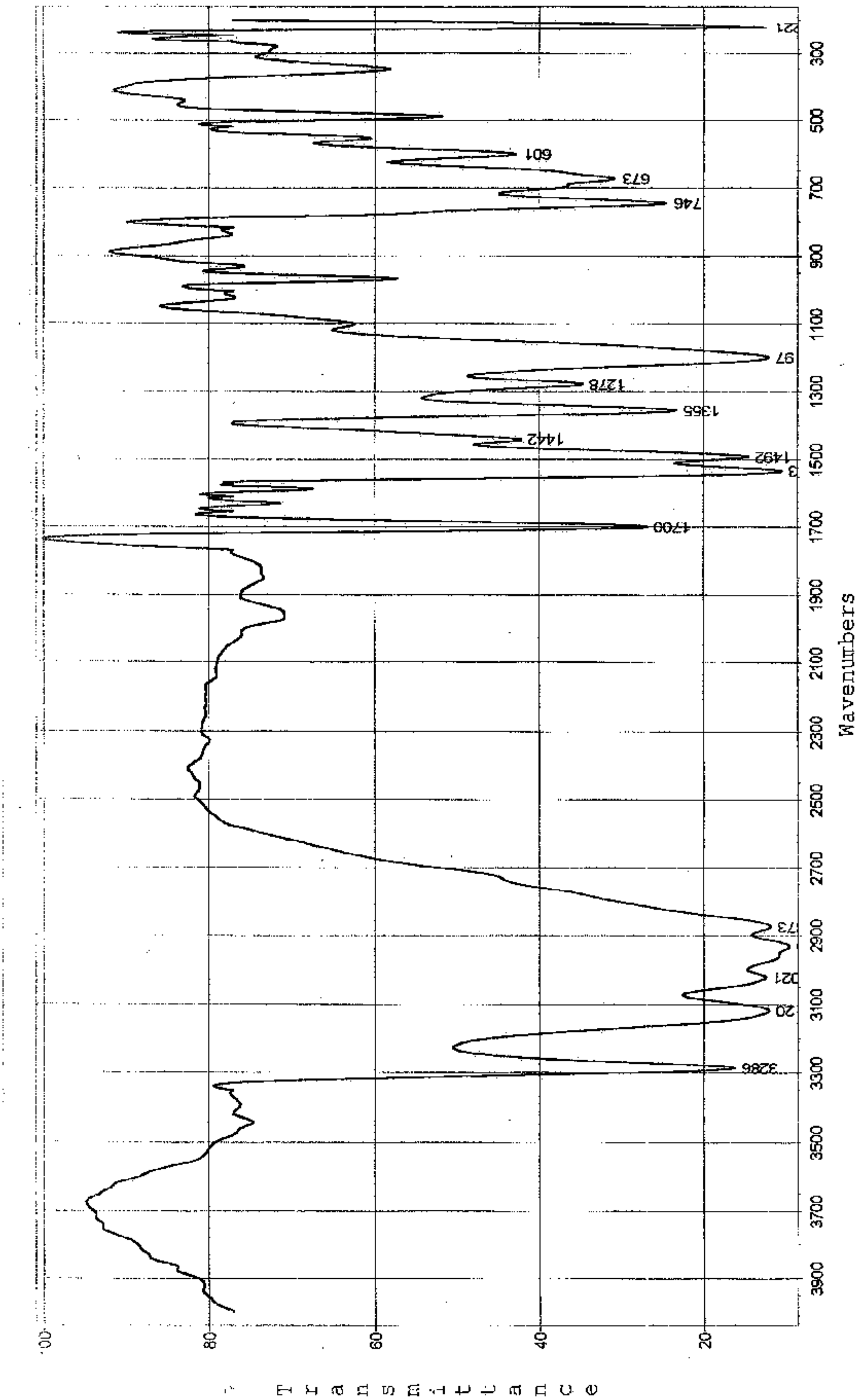


Fig. 20. IR spectrum of N–{[(phenylamino) thioxomethyl] hydrazinocarbonylmethyl} pyridinium chloride (PTHPC) in KBr.

The ^{1}H–NMR spectra of PTHPC in d_6-DMSO (Figs. 21 and 22) show three singlet signals at 11.13, 10.09 and 9.88 p.p.m., downfield with respect to TMS, assignable to the protons of NH(1), NH(2) and NH(4) vibrations, respectively. The singlet signal at 5.75 p.p.m. is attributed to the protons of CH_2 of the (N-CH_2) group. The multiple signals in the 7.17- 9.17 p.p.m. region are attributed to the protons of the pyridyl and phenyl groups. The latter signals are commensurate with ten protons and are assigned to the protons of the pyridyl and phenyl groups.

4. Characterization of the Solid Metal Complexes Derived by Conventional Chemical Method.

4.1. Spectral, Conductance and Magnetic Moments for the Cu(II) Complexes Derived from 3-MPTU and 6- MPTU.

The molar conductance value for the olive green complex, $[Cu(C_{13}H_{13}N_3S)_2Cl.H_2O]Cl$, in DMF was found to be 33.7 $\Omega^{-1}.cm^2.mol^{-1}$ indicating the electrolytic nature of this complex with one chloride ion resides outside the coordination sphere(41). On comparing the IR spectra of this complex in Nujol mull (Fig.23) with the free ligand (Fig.8), we observed the negative shifts of the bands due to υ(C=N) and υ(C=C) vibrations for the pyridyl group as well as the thioketo group (C=S) to lower wavenumbers. These bands are observed at 1610, 1550, 1527, 1457, 1176 and 750 cm^{-1} in the spectrum of the Cu(II) complex while it observed at 1631, 1592, 1570, 1511, 1255 and 742 cm^{-1} in

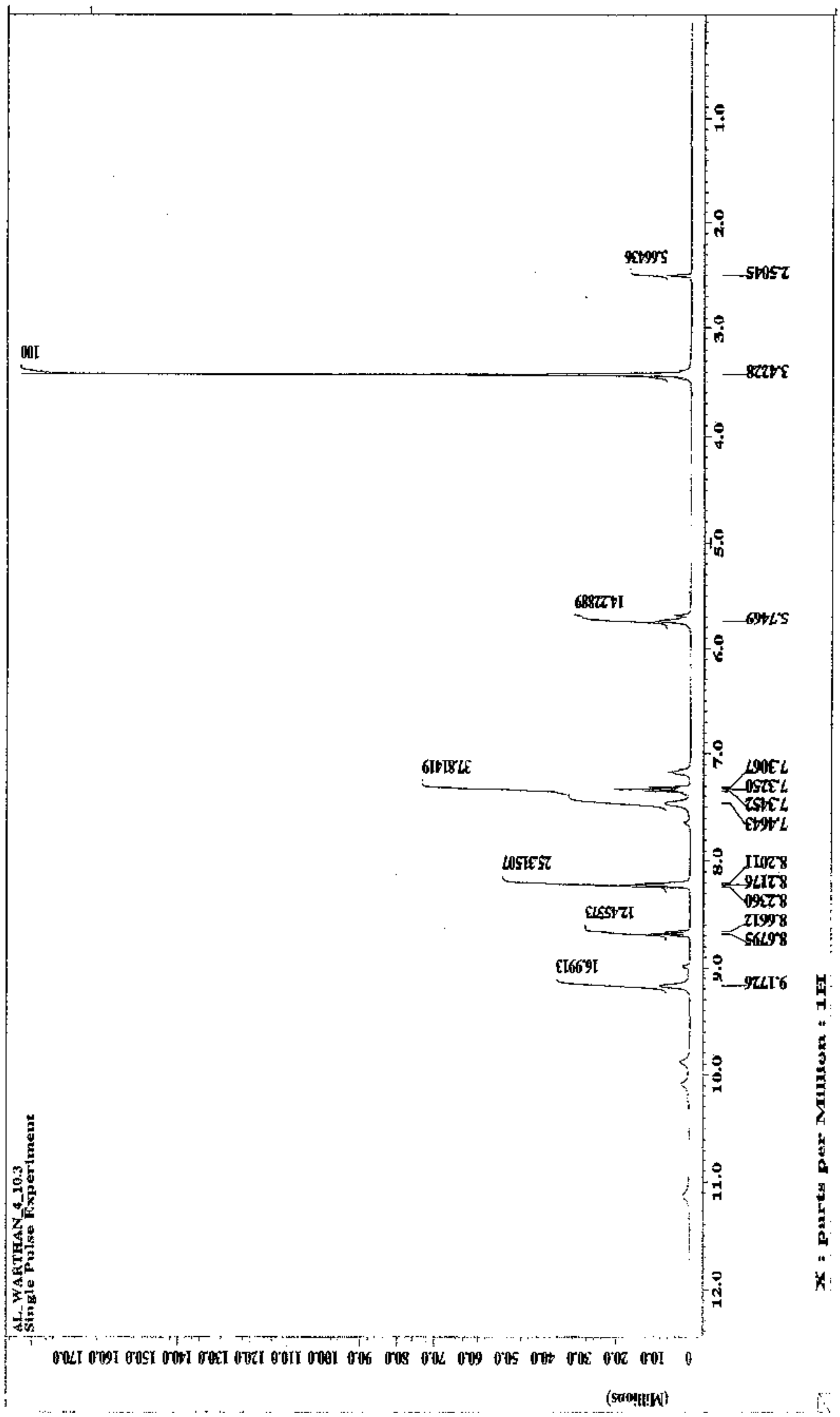


Fig. 21. ^{1}**H-NMR spectrum of N-{[(phenylamino) thioxomethyl] hydrazinocarbonylmethyl} pyridinium chloride (PTHPC) in d_6-DMSO.**

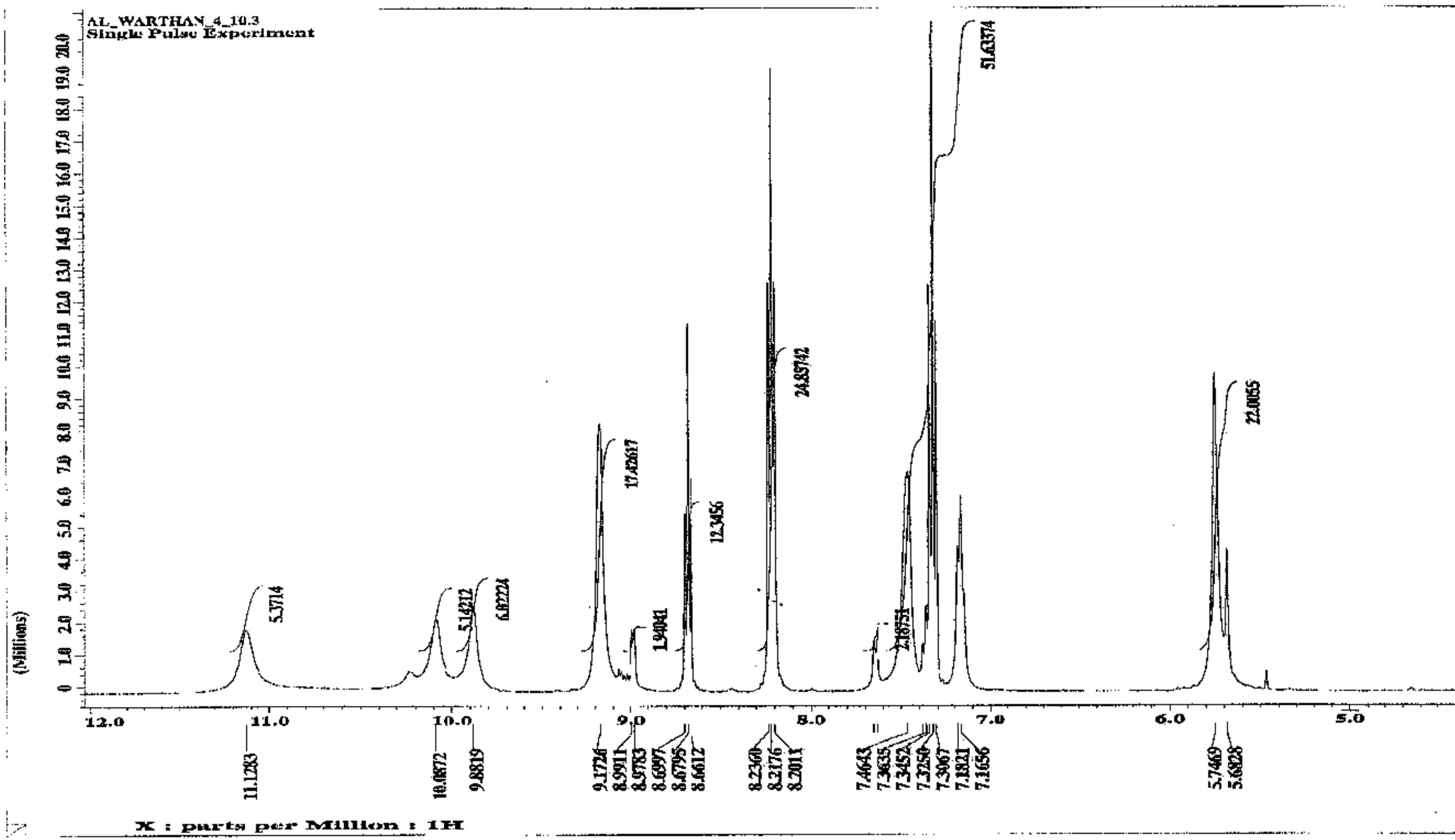


Fig. 22. ^{1}H-NMR spectrum of N-{[(phenylamino) thioxomethyl] hydazinocarbonylmethyl} pyridinium chloride (PTHPC) in d_6-DMSO.

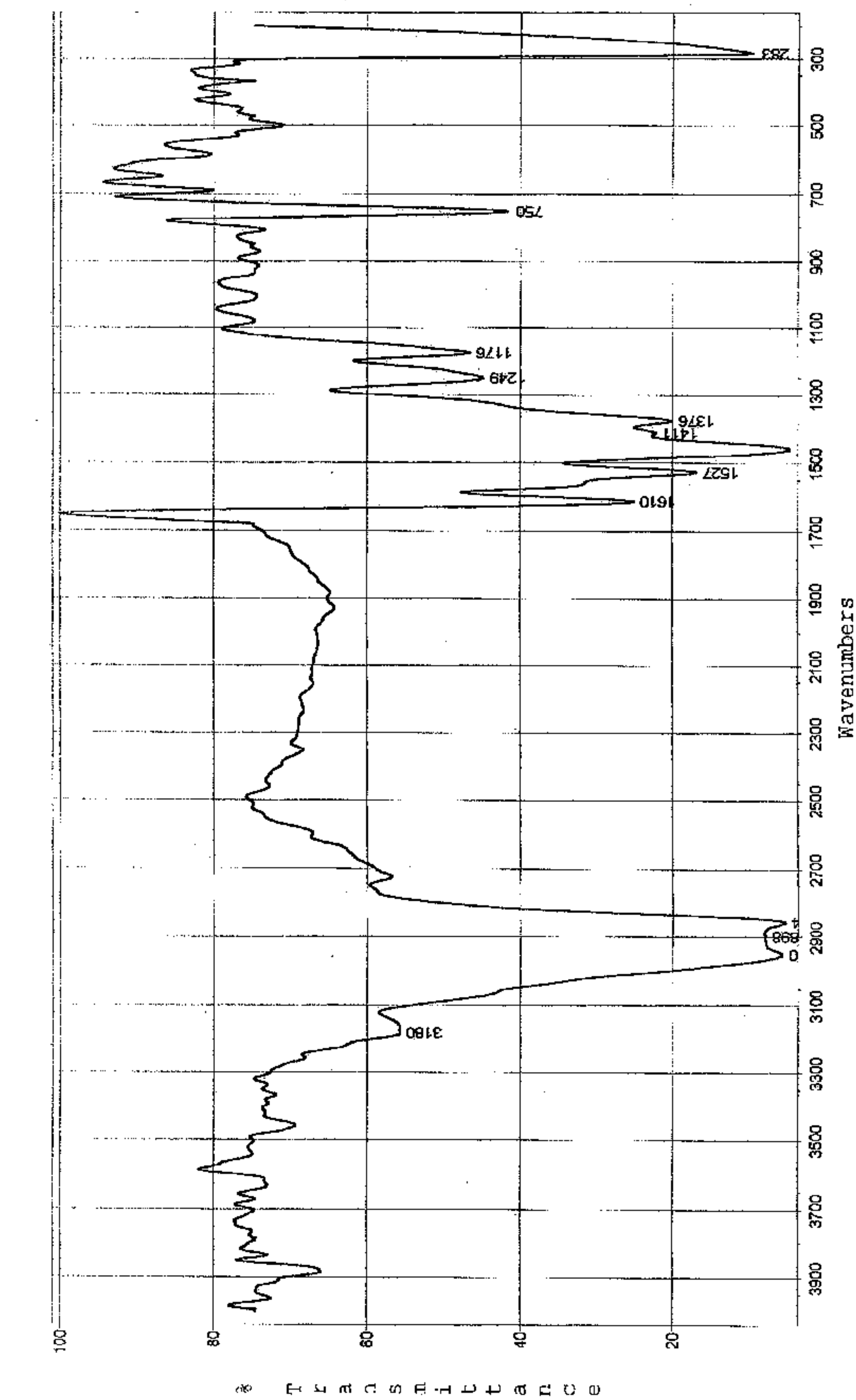
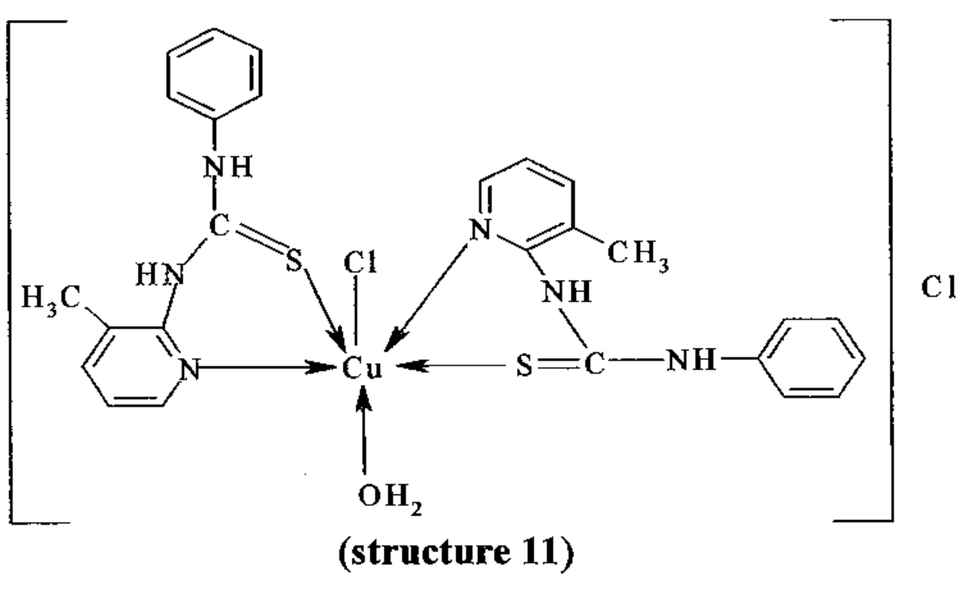


Fig. 23. Infrared spectrum of $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl$ in Nujol mull.

the spectrum of the free ligand. This suggests that the ligand (3-MPTU) acts in a bidentate fashion coordinating *via* the pyridyl nitrogen and CS groups forming a six-member ring around the Cu(II) ion. Also, the spectrum (Fig.23) shows three new bands at 480, 330 and 283 cm^{-1} assigned to υ(Cu-O)[42], υ(OH)(H_2O) vibrations. Moreover, the bands due to NH(1) and NH(2) are shifted to lower wavenumbers and observed at 3260 and 3180 cm^{-1}, respectively. Doubtless the shifts of those bands confirm the participation of the thioketo group in bonding and hence it affects on its neighbour NH bands.

The electronic spectrum of the Cu(II) complex in Nujol mull, (Fig.24) shows a broad band centered at 12450 cm^{-1} (803 nm). This band is attributed to $^2E_g \longrightarrow {}^2T_{2g}$ transition in a distorted-octahedral environment around the Cu(II) ion[45]. The value of magnetic moment at room temperature (1.68 B.M.) suggests the existence of monomeric form and the absence of any copper–copper interactions[46]. All these foundations suggest structure 11 for this complex.



(structure 11)

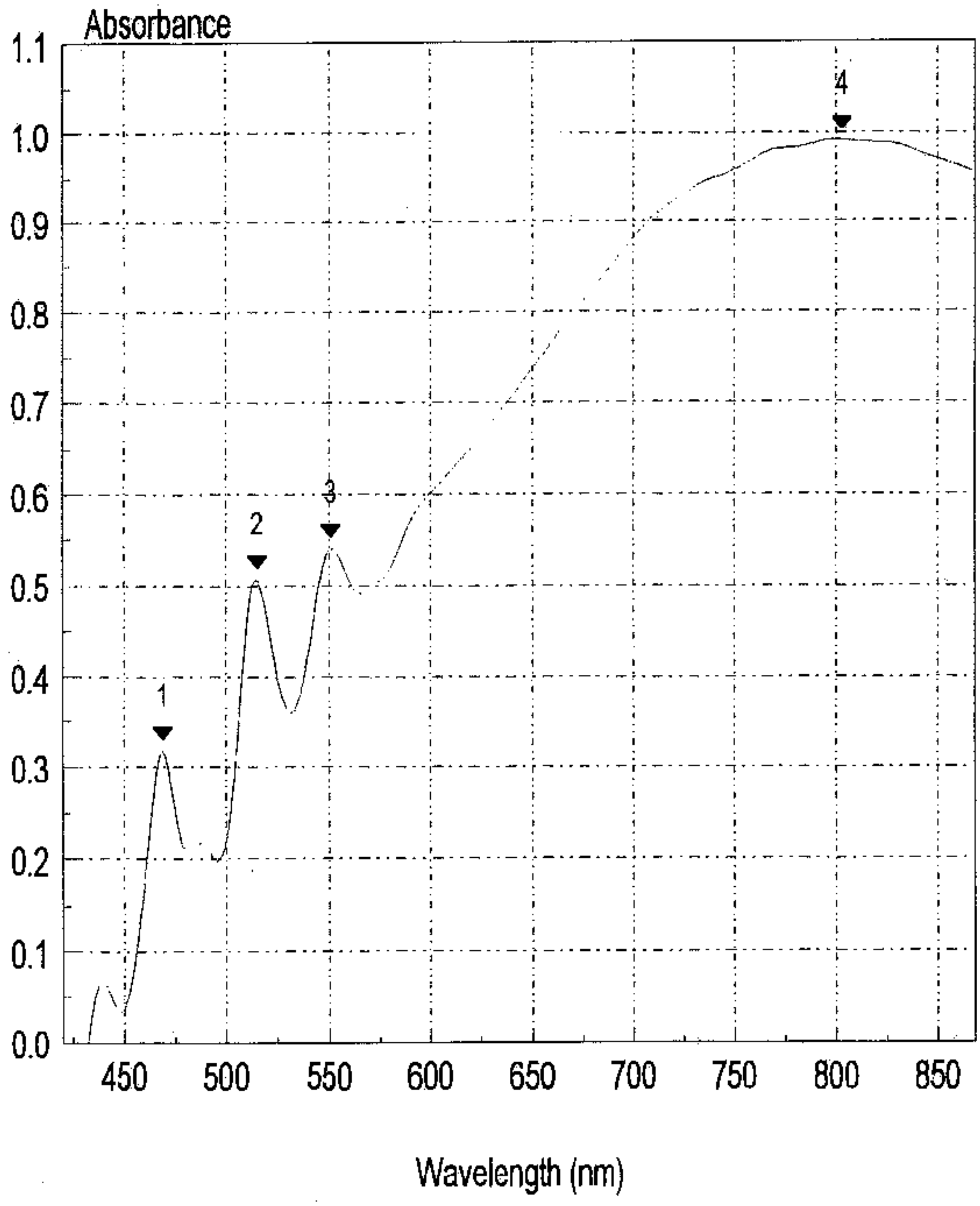


Fig. 24. Electronic spectrum of $[Co(C_{13}H_{12}N_2OS)_2\ Cl.H_2O]Cl$ in Nujol mull.

The value of molar conductance (8.3 $\Omega^{-1}.cm^{-1}.mol^{-1}$) for the yellowish-green complex, $[Cu(C_{13}H_{13}H_{13}N_3S)Cl_2]$, in DMF suggests a non-electrolytic nature of this complex[41]. The IR spectrum of this complex in Nujol mull (Fig.25) indicates the involvement of both the pyridyl nitrogen and the thioketo groups in bonding forming a six-member ring around the Cu(II) ion. These groups (CN and CS) are shifted to lower wavenumbers and are observed at 1627, 1560, 1535, 1515, 1216 and 754 cm^{-1} in comparison to these observed at 1631, 1592, 1571, 1511, 1251 and 742 cm^{-1} in the spectrum of the free ligand (Fig.10). Also, the NH(1) and NH(2) bands are observed at 3444 and 3342 cm^{-1} suggesting the obscure of the hydrogen bonding exists in the free ligand as well as the participation of thioketo group in bonding .

Also, new bands are observed at 432, 368 and 341 cm^{-1} assigned to υ(Cu-N)[43] and υ(Cu–Cl)[42,44] vibrations, respectively. The existence of two Cu-Cl bands indicates that the two chloride ions are existed in a cis-form[47].

The electronic spectrum of the Cu(II) complex (Fig.26) in Nujol mull shows two bands at 14430 cm^{-1} (693 nm) and 17575 cm^{-1} (569 nm) assigned to $^2T_{2g} \longrightarrow {}^2E_{2g}$ transition in a pseudo–tetrahedral arrangement around the Cu(II) ion[48]. The value of magnetic moment (1.60 B.M.) suggests the absence of any copper-copper interaction[46]. The results suggest structure 12 for this complex.

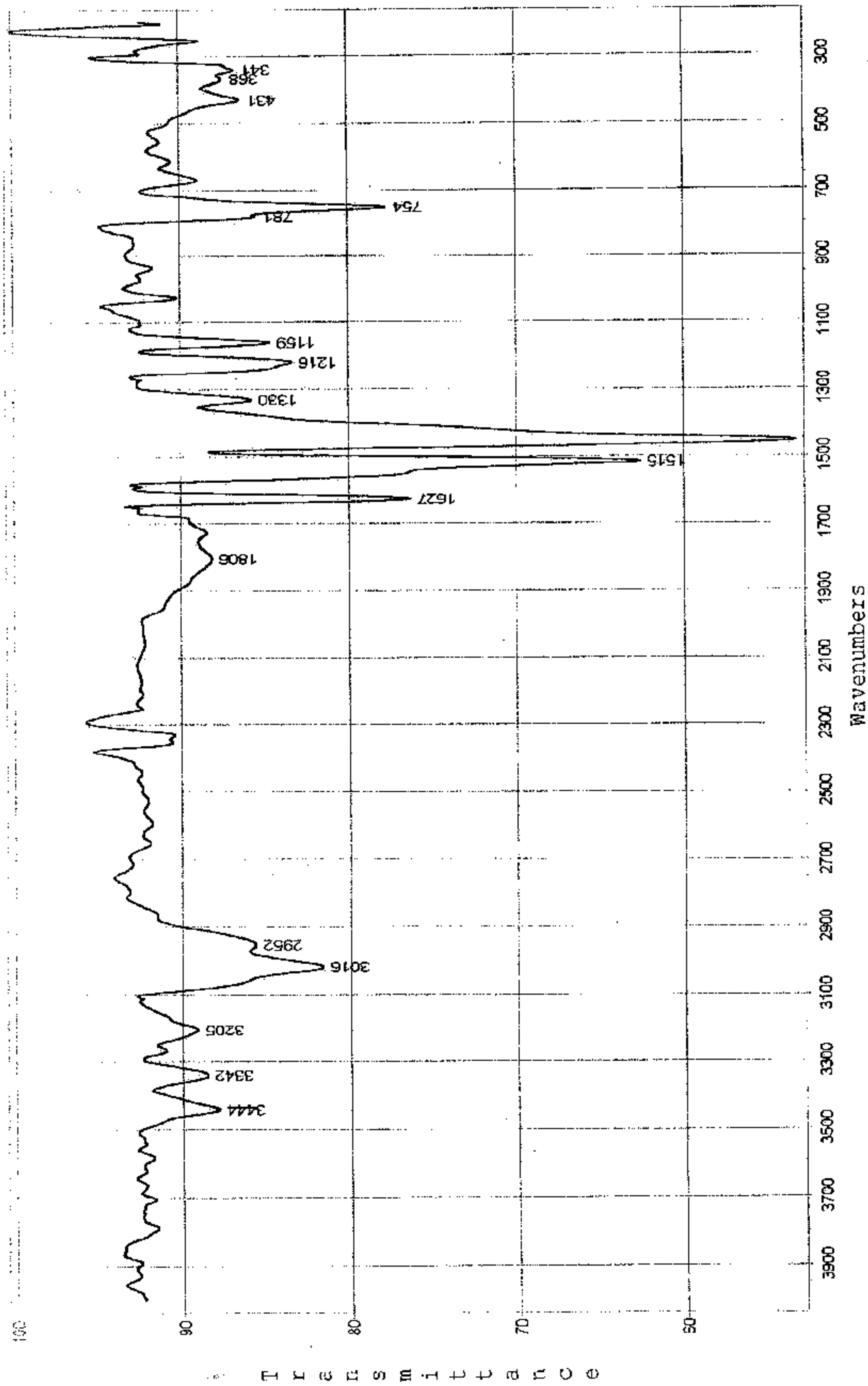


Fig. 25. Infrared spectrum of [Cu($C_{13}H_{13}$ N_3S)Cl_2] in Nujol mull.

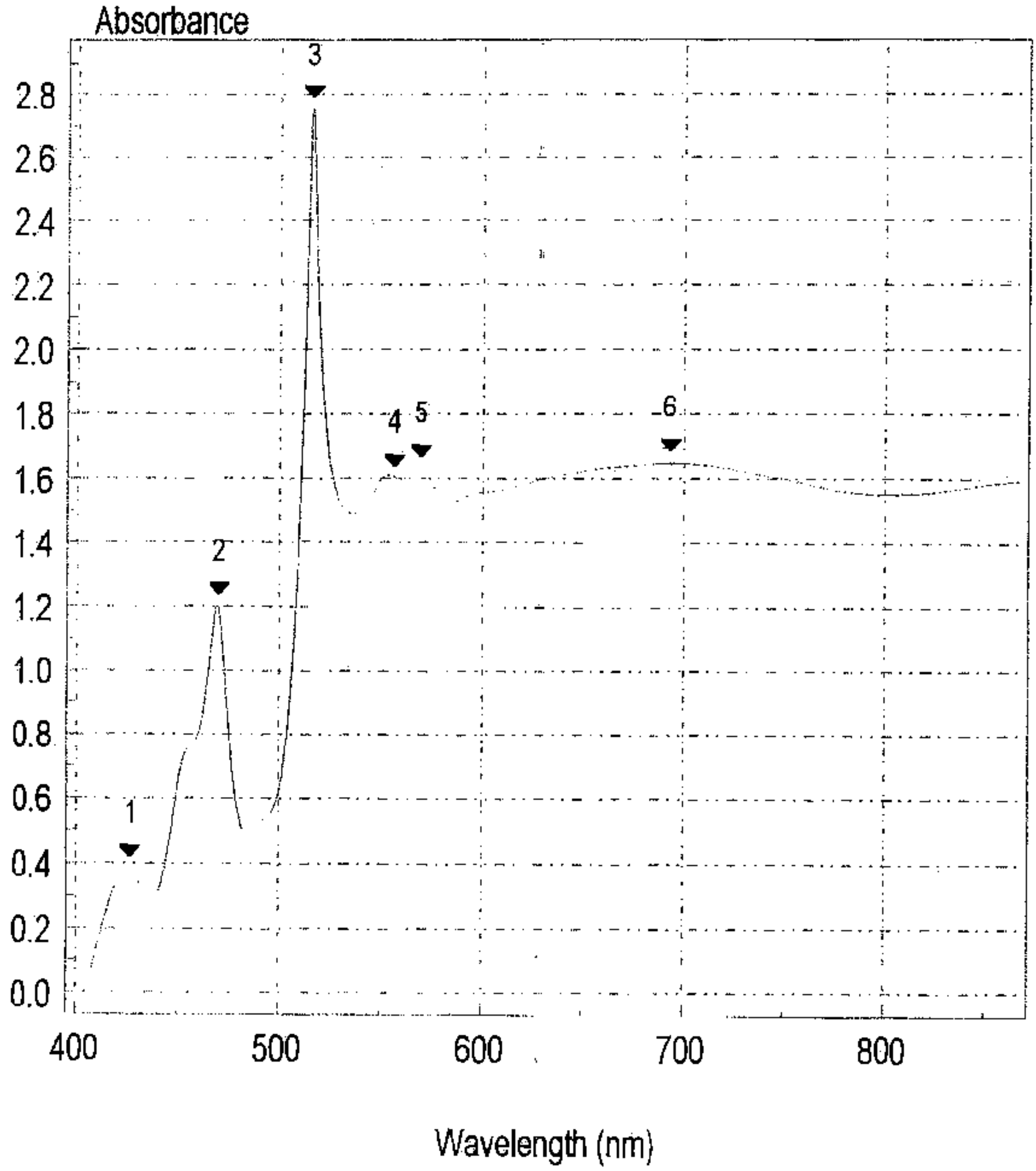
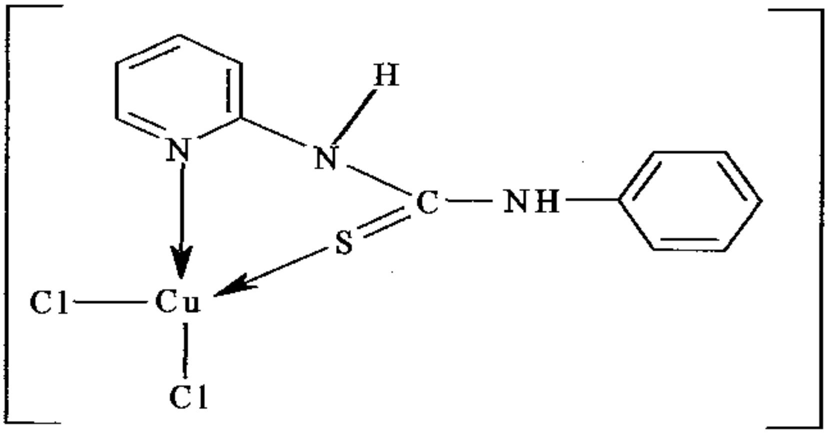


Fig. 26. Electronic spectrum of [Cu($C_{13}H_{13}N_3S$)Cl_2] in Nujol mull.



(structure 12)

The IR spectrum of the petrol complex, $[Co(C_{13}H_{13}N_3S)Cl_2]$. $1/2H_2O.1/2EtOH$, is quite similar to the Cu(II) complex (Fig.25). This suggests that the ligand (3-MPTU) coordinates to the Co(II) ion in a bidentate manner through the pyridyl nitrogen and thioketo groups forming a six-member ring around the Co(II) ion.

The value of molar conductance in DMF (6.3 $\Omega^{-1}.cm^2.mol^1$) suggests a non-electrolytic nature of this complex(41). The electronic spectrum of the Co(II) complex in Nujol mull (Fig. 27) shows three bands at 12903 cm^{-1} (775 nm), 15873 cm^{-1} (630 nm) and 16807 cm^{-1} (595 nm) assigned to $^4A_2 \longrightarrow {}^4T_1$ (P) transitions in a tetrahedral geometry around the Co(II) ion(49,50). The value of magnetic moment (4.1 B.M.) is taken as evidence for the existence of tetrahedral geometry around the Co(II) ion(50). All these foundations suggest structure 13 for the Co(II) complex.

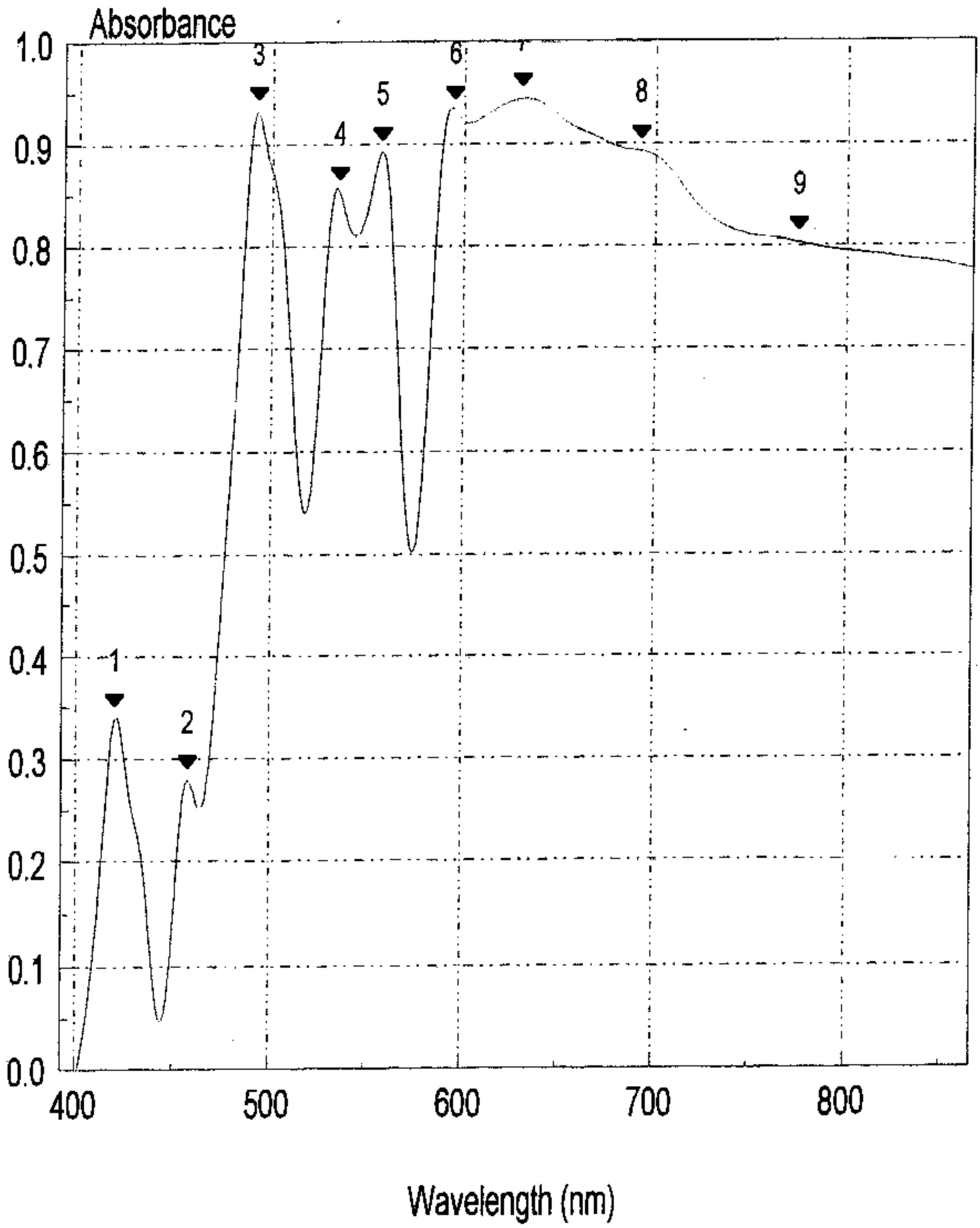
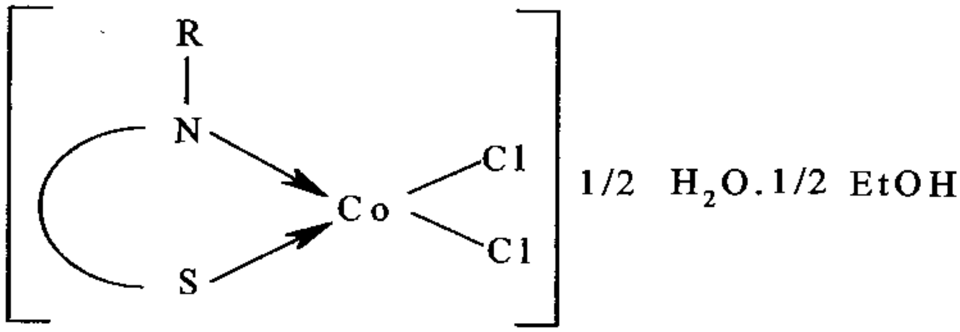


Fig. 27. Electronic spectrum of [Co($C_{13}H_{13}$ N_3S)Cl_2]1/2 H_2O.1/2EtOH in Nujol mull.



R = - NH-Ph

(structure 13)

The molar conductivity value for the blue Co(II) complex, $[Co(C_{13}H_{13}N_3S)_2]Cl_2.1/2H_2O$, in DMF was found to be 76.2 $\Omega^{-1}.cm^2.mol^{-1}$ suggesting the electrolytic nature of this complex with two chloride ions outside the coordination sphere[(41)]. The IR spectrum of the Co(II) complex is similar to the previous Cu(II) complex and the ligand (6-MPTU) coordinates in a bidentate manner *via* the pyridyl nitrogen and the thioketo groups forming a six–member ring around the Co(II) complex. The electronic spectrum of the Co(II) complex in Nujol mull (Fig.28) shows three bands at 12970 cm^{-1} (771 nm), 15825 cm^{-1} (632 nm) and 16835 cm^{-1} (594 nm) assigned to $^4A_2 \rightarrow ^4T_1(P)$ transitions in a tetrahedral geometry around the Co(II) ion[(49.50)]. The value of magnetic moment (4.5 B.M.) is taken as evidence for the existence of tetrahedral geometry around the Co(II) ion[(50)]. The results suggest structure 14 for the Co(II) complex.

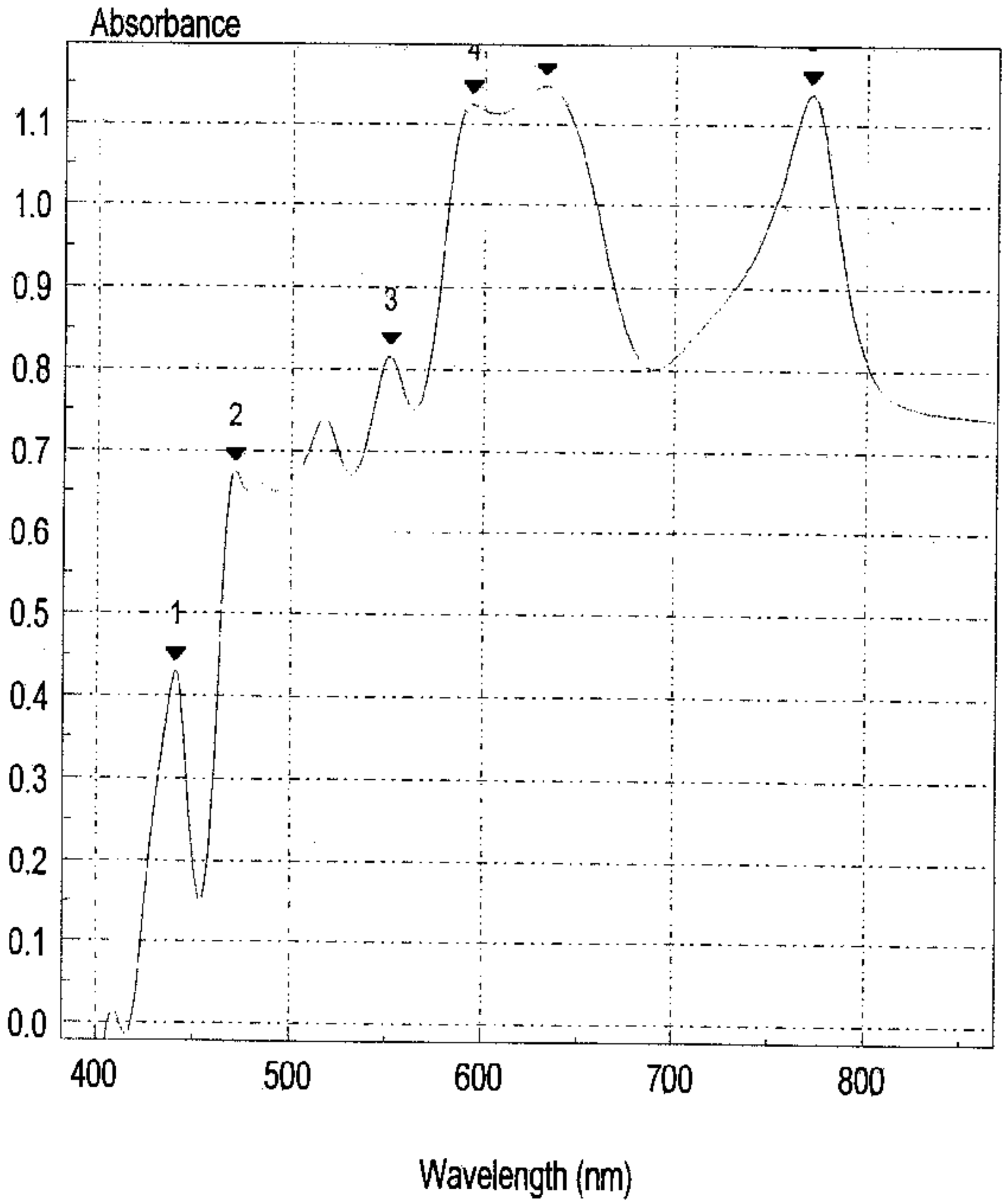
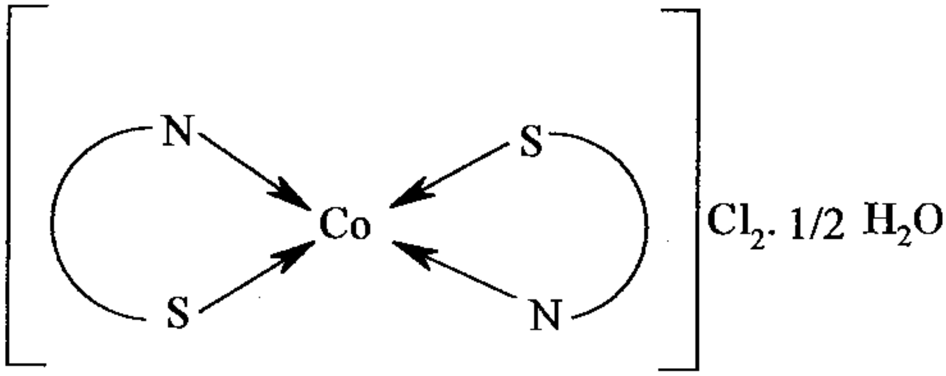


Fig. 28. Electronic spectrum of $[Co(C_{13}H_{13}N_3S)_2Cl_2]1/2\ H_2O$ in Nujol mull.



(structure 14)

4.2. Spectral, Conductance and Magnetic Moments for the Cu(II) and Co(II) Complexes Derived from G.P.

The IR spectra of the Cu(II) and Co(II) complexes derived from G.P. in Nujol mull are more or less the same and we are represented all by Fig. 29. On comparing the IR spectra of the Co(II) complex, $[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$, (Fig. 29) with the free ligand (Fig. 1), we observed that the bands due to the NH_2 and carbonyl oxygen groups are shifted to lower wavenumbers. The bands at 3459, 3343, 3320, 1693 and 1635 cm^{-1}, assigned to $\upsilon_{as}(NH_2)$, $\upsilon_s(NH_2)$, $\upsilon(NH)$, $\upsilon(CO)$ and $\beta(NH_2)$, vibrations in the free ligand (G.P), are observed at 3405, 3372, 3264, 1652 and 1610 cm^{-1} in the spectrum of the Co(II) complex (Fig. 29). The broad weak bands observed in the 1900-2100 and 2300-2500 cm^{-1} regions, assigned to the existence of hydrogen bonding, are obscured in the spectrum of the Co(II) complex suggesting the destruction of hydrogen bonding on chelating.

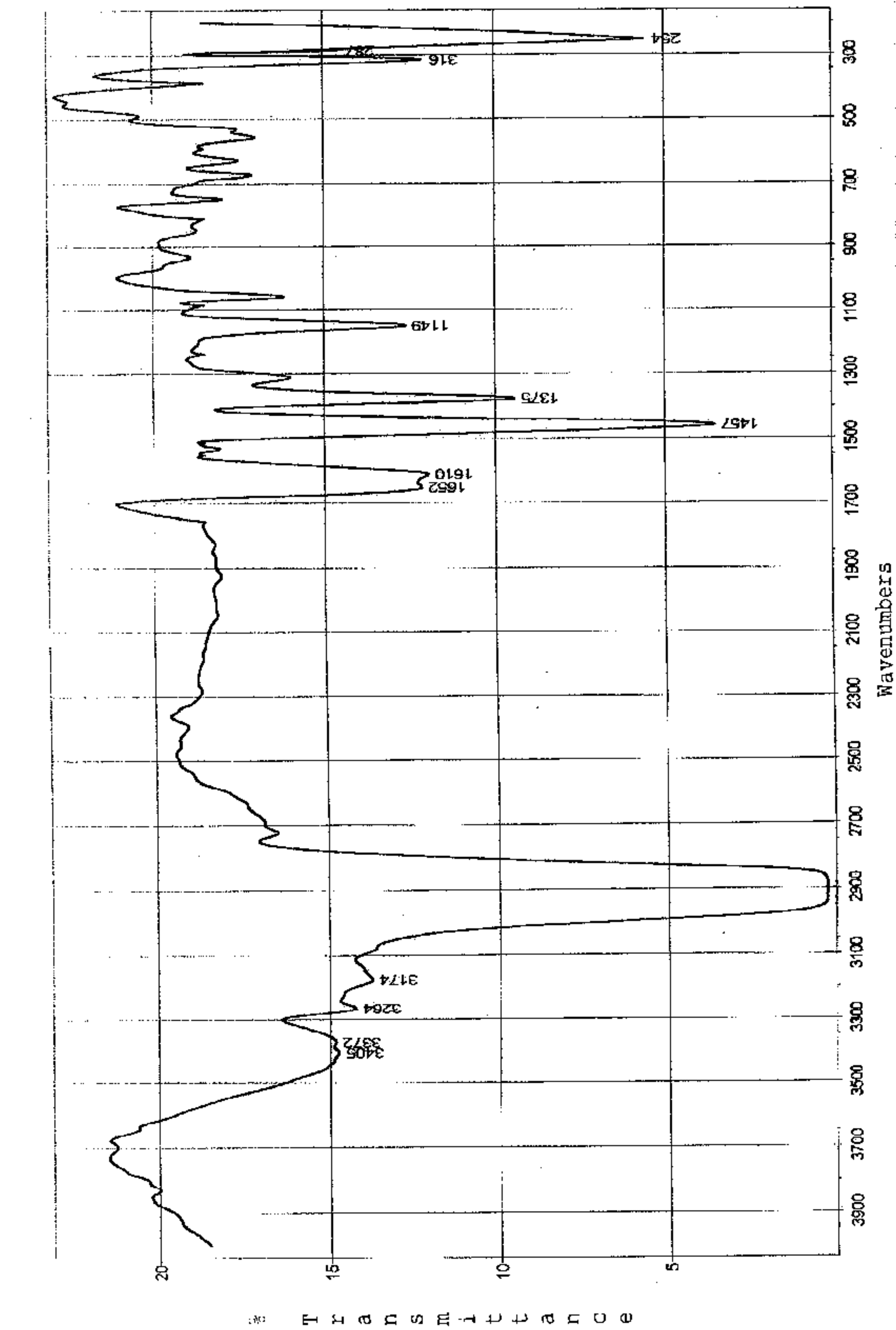
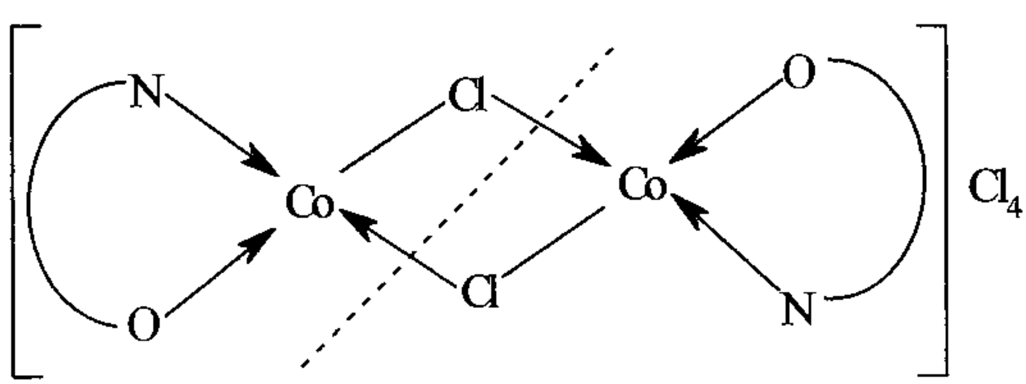


Fig. 29. Infrared spectrum of $[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$ in Nujol mull.

The new four bands at 254, 287, 350 and 430 cm^{-1} are assigned to υ(Co-O)[42], υ(Co-N)[43] and υ(Co-O)[42] vibrations, respectively. The observation of two Co–Cl bands suggests that the two chloride ions around the cobalt (II) ion are not identical and exist in a dimeric structure. The high value of molar conductance in DMF (169.2 $\Omega^{-1}.cm^{-1}.mol^{-1}$) suggests the existence of four chloride ions outside the coordination sphere[41].

The electronic spectrum of the Co(II) complex in Nujol mull (Fig. 30) shows three bands at 14450 cm^{-1} (692 nm), 15083 cm^{-1} (663 nm) and 159074 cm^{-1} (626 nm) assigned to $^4A_2 \longrightarrow {}^4T_1$ (P) transitions in a tetrahedral geometry around the Co(II) ion[49,50]. The blue colour of this complex as well as the value of magnetic moment (4.2 B.M.) are taken an evidences of the presence of tetrahedral structure around the Co(II) ion[50]. All these foundations suggest structure 15 for this complex.



(structure 15)

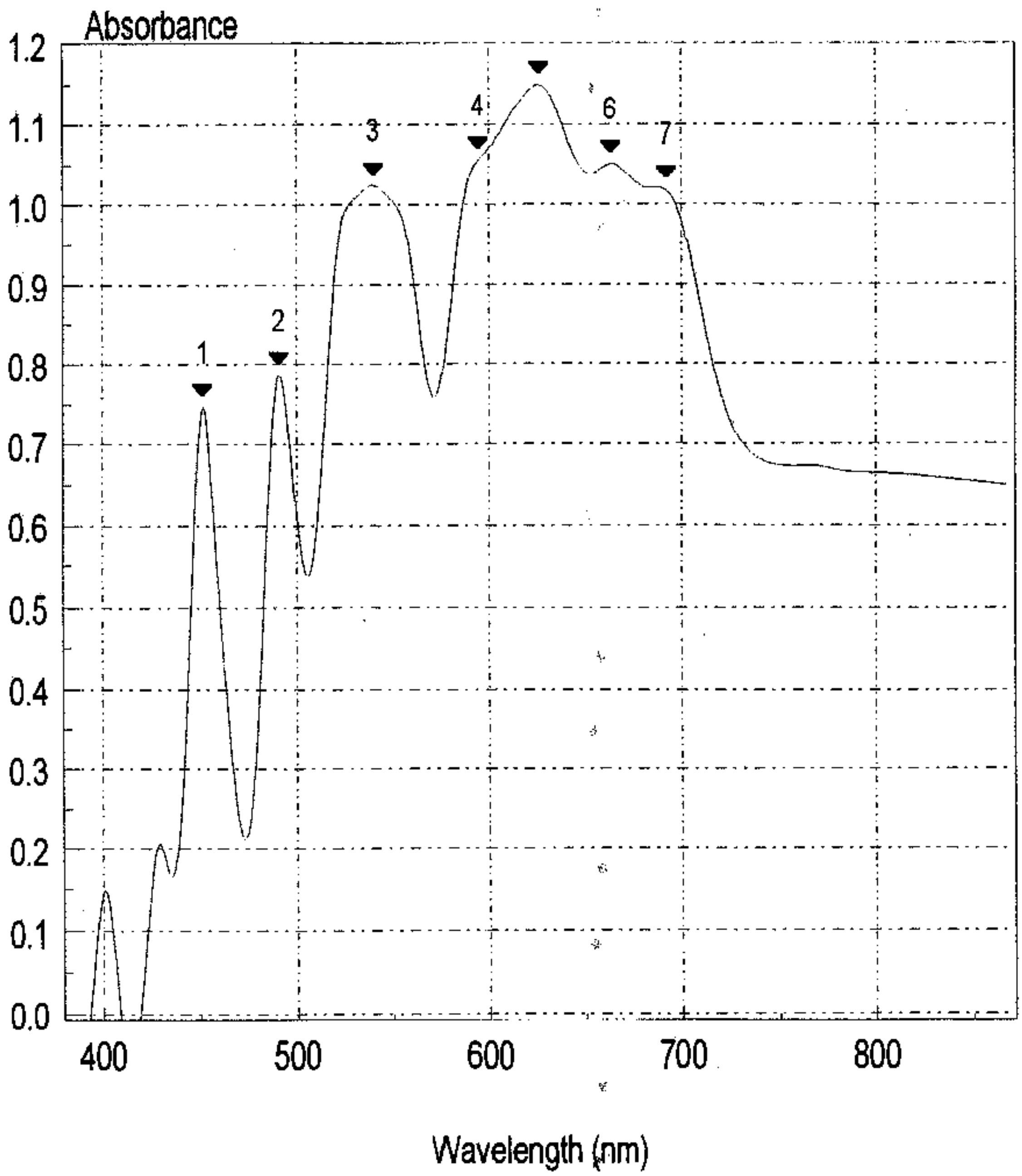
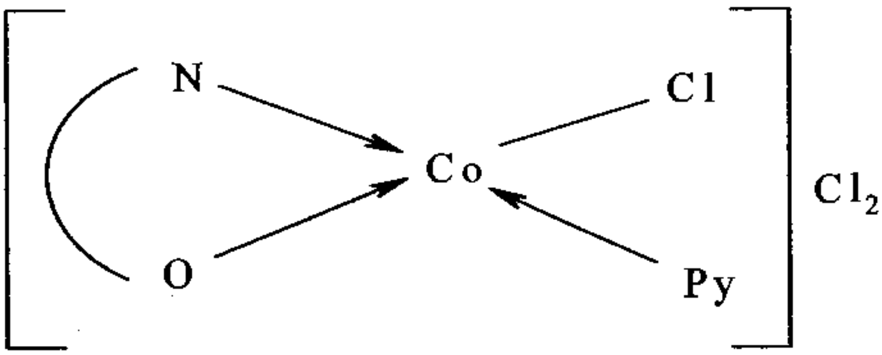


Fig. 30. Electronic spectrum of $[Co_2(C_7H_{10}N_3O)_2Cl_2]Cl_4$ in Nujol mull.

On adding pyridine to the Co(II) complex a new complex is formed due to the destruction of chlorine bridge with substitution of one pyridine molecule as shown in structure 16.



(structure 16)

The value of molar conductance for the Cu(II) complex, $[Cu_2(C_7H_{10}N_3O)_2Cl_2]Cl_4.2EtOH$, in DMF was found to be 155.8 $\Omega^{-1}.cm^2.mol^{-1}$. This indicates the electrolytic nature of this complex and the existence of four chloride ions outside the coordination sphere(41). The electronic spectrum of the Cu(II) complex (Fig. 31) shows three bands at 11976 cm^{-1} (835 nm), 14388 cm^{-1} (695 nm) and 16949 cm^{-1} (590 nm) assigned to transitions within the spinor components of ^2D in a D_{2d} field(51). The value of magnetic moment (1.63 B.M.) supports the absence of any copper-copper interaction(46). The structure of this complex is similar to structure 15 and the existence of chlorine bridge is confirmed by adding pyridine which gives a complex similar to structure 15.

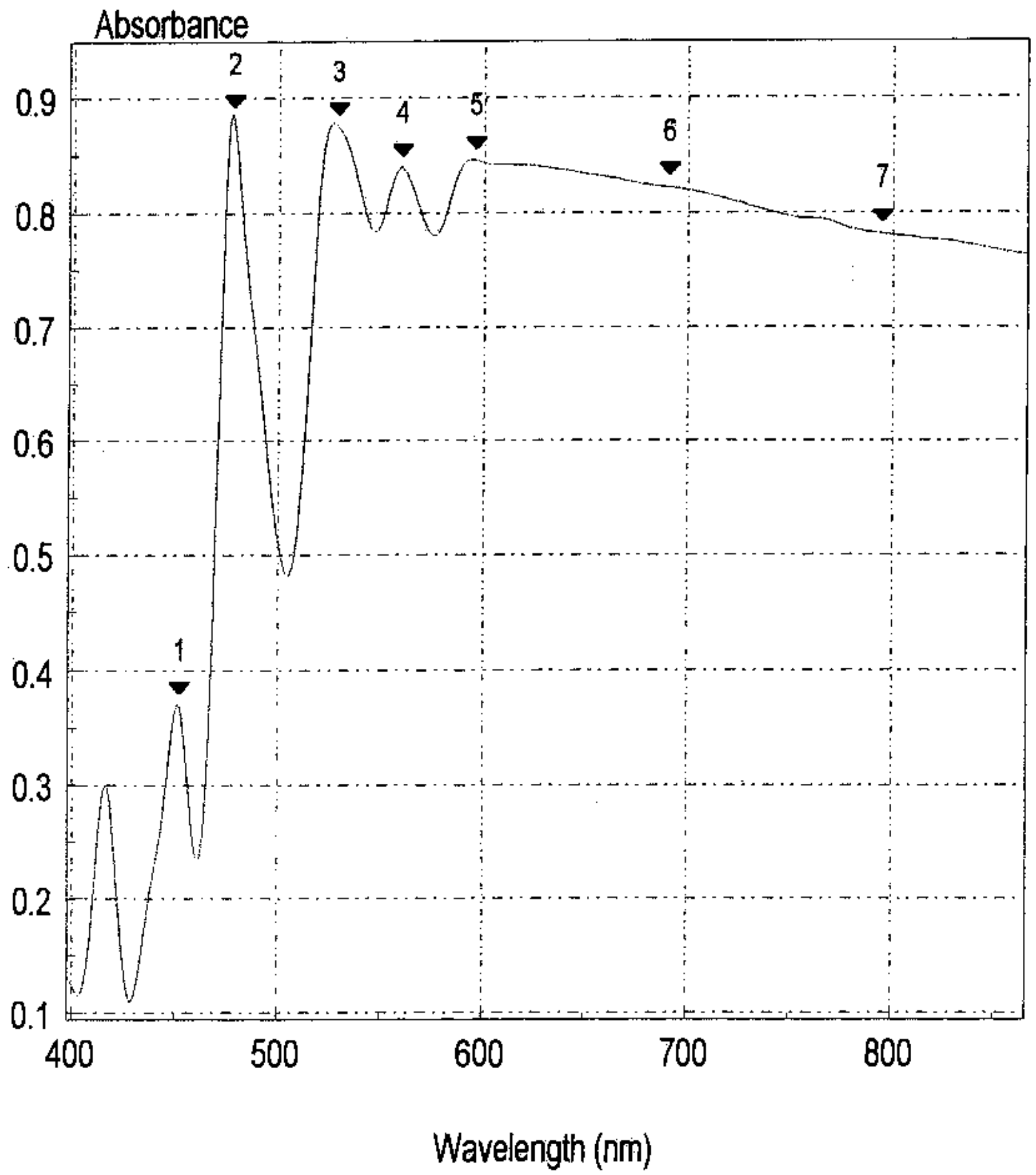
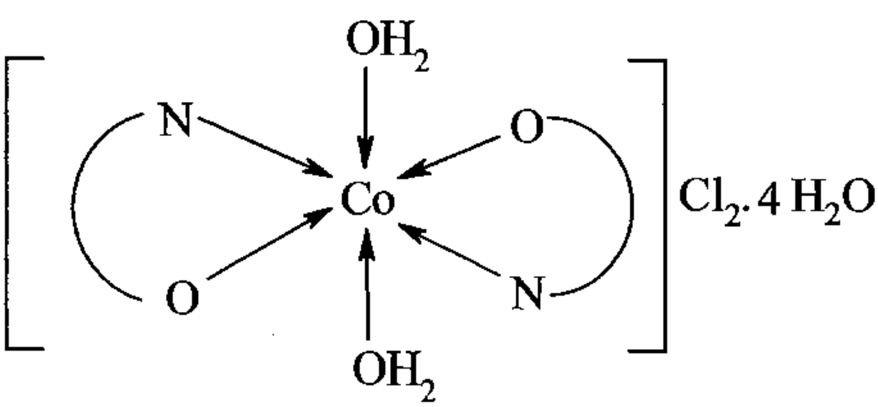


Fig. 31. Electronic spectrum of $[Cu_2(C_7H_{10}N_3O)_2Cl_2]Cl_4.EtOH$ in Nujol mull.

On the other hand, the green Cu(II) complex with the formula, $[Cu_2(C_7H_9N_3O)_2Cl_2.(H_2O)_2(EtOH)_2]Cl_2$, shows an distorted–octahedral geometry around the Cu(II) ion. The electronic spectrum in Nujol mull (Fig. 32) shows only one broad band centered at 12804 cm^{-1} (781 nm) attributable to $^2E_g \longrightarrow {}^2T_g$ transition(45). Also, the value of magnetic moment (1.56 B.M) is very near to that reported for Cu(II) and contains no copper-copper interactions(46).

Finally, the electronic spectrum of the violet Co(II) complex, $[(Co(C_7H_9N_3O)_2(H_2O)_2]Cl_2.4H_2O$, in Nujol mull (Fig. 33) shows two bands at 16920 cm^{-1} (691 nm) and 20450 cm^{-1} (481 nm) assigned to $^4T_{1g} \longrightarrow {}^4A_{2g}$ and $^4T_{1g} \longrightarrow {}^4T_{1g}$ (P) transitions in an octahedral geometry around the Co(II) ion(52). The molar conductance value (70.2 $\Omega^{-1}.cm^2.mol^{-1}$) suggests 1:2 electrolyte(41). The magnetic moment value (5.1 B.M.) is taken as evidence for the existence of octahedral geometry around the Co(II) ion(50). All these foundations suggest structure (17) for the Co(II) complex.



(structure 17)

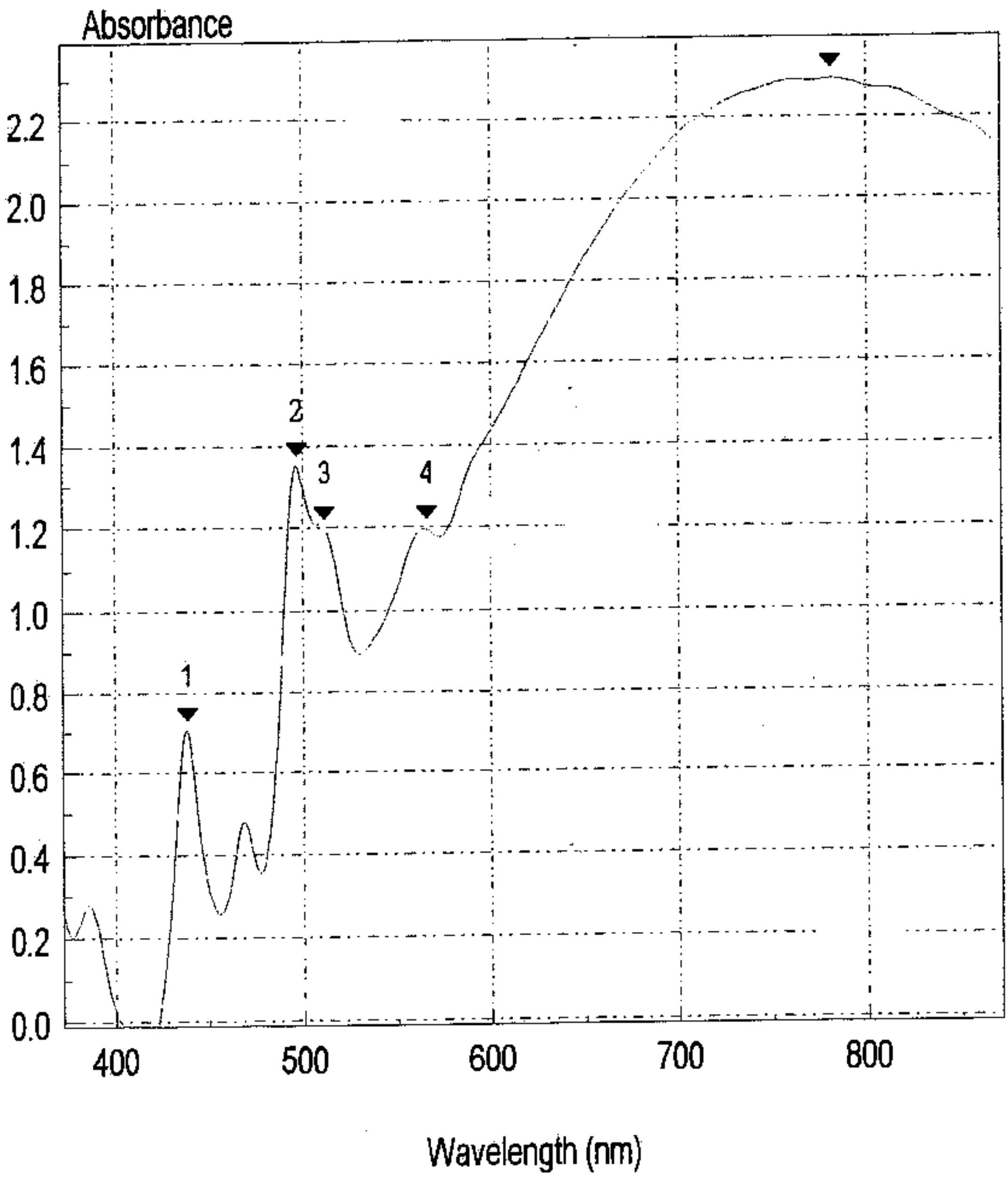


Fig. 32. Electronic spectrum of $[Cu_2(C_7H_9N_3O)_2Cl_2.(H_2O)_2(EtOH)_2]Cl_2$ in Nujol mull.

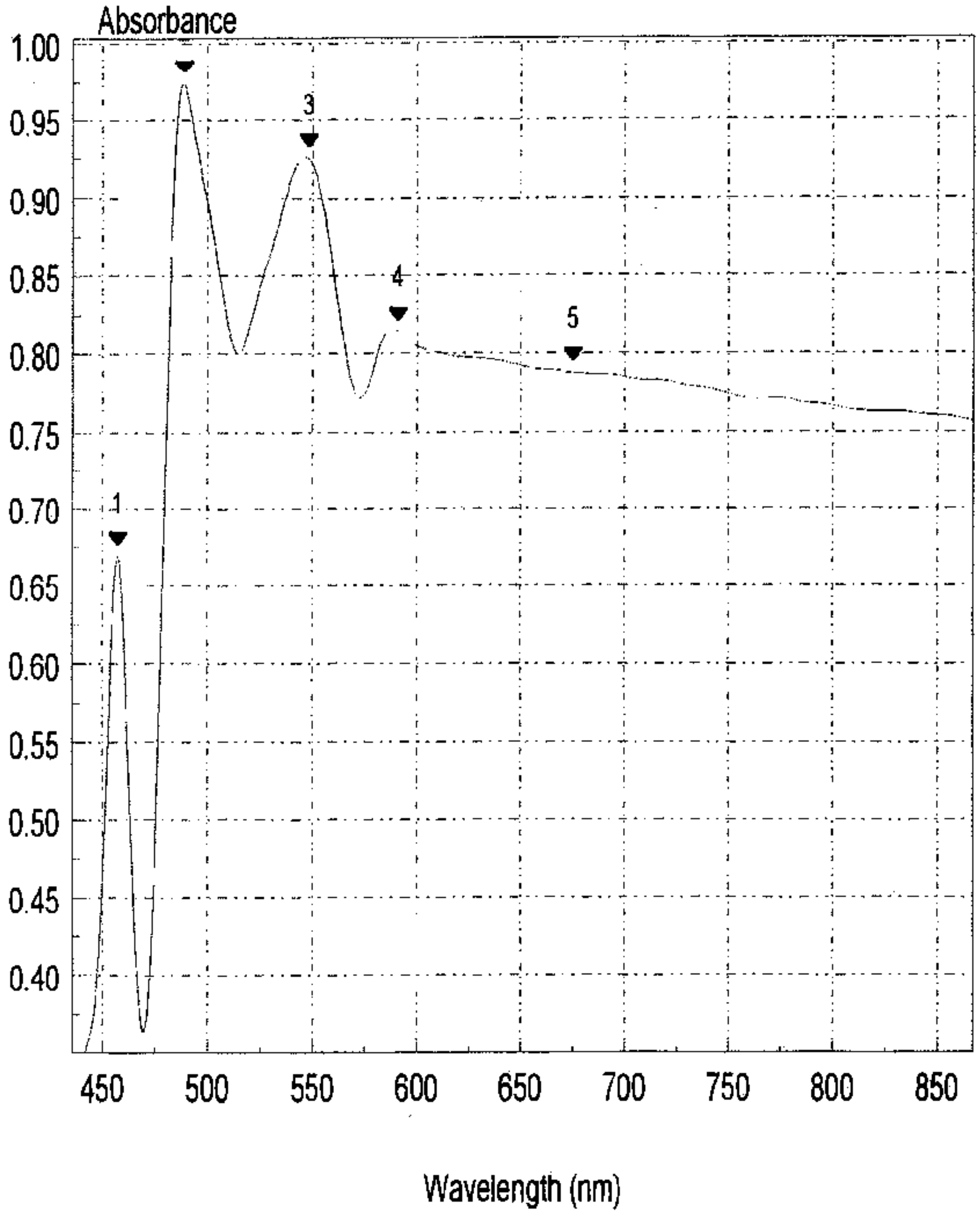


Fig. 33. Electronic spectrum of $[Co(C_7H_9N_3O)_2(H_2O)_2]Cl_2.4H_2O$ in Nujol mull.

4.3. Spectral, Conductance and Magnetic Moments for the Cu(II) and Co(II) Complexes Derived from HPPTU and 3-HPPTU.

Four different Co(II) and Cu(II) complexes have been isolated from HPPTU and 3-HPPTU with the general formulae, $[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$, $[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$, $[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$ and $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$. The former complex is isolated in which the ligand (HPPTU) coordinates in a bidentate manner with displacement of a hydrogen atom from the OH group. On the other hand, the latter three complexes are isolated without displacement the hydrogen atom.

The first blue Co(II) complex, $[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$, shows a value of molar conductance (9.3 $\Omega^{-1}.cm^{-1}.mol^{-1}$) indicating a non-electrolytic nature of this complex in DMF[41]. On comparing the IR spectrum of this complex in Nujol mull (Fig. 34) with the free ligand, HPPTU (Fig. 4), we observed the appearance of several strong bands in the 3556-3200 cm^{-1} region. These bands are assigned to υOH (EtOH), υ^1NH (free), υ^2NH (free), υ^1NH (hydrogen-bonded) and υ^2NH (hydrogen – bonded) vibrations, respectively. The observation of the bands at 1544, 1502 and 1456 cm^{-1} due to υ(-N-C=S) vibrations[33,34] as well as the bands at 1250 and 744 cm^{-1} assigned to υ(C=S) vibration, suggests that the thioketo group does not taking part in coordination.

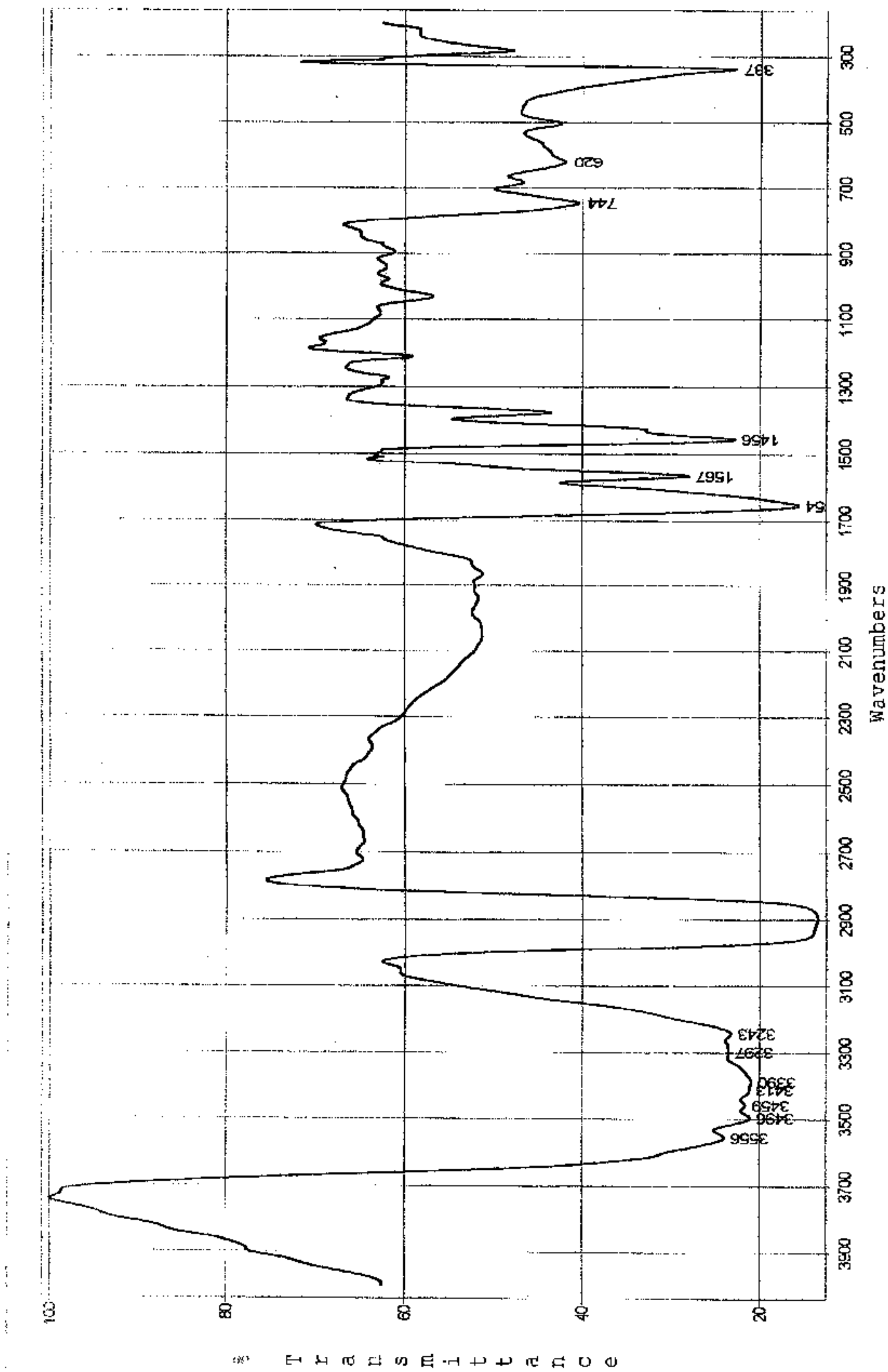
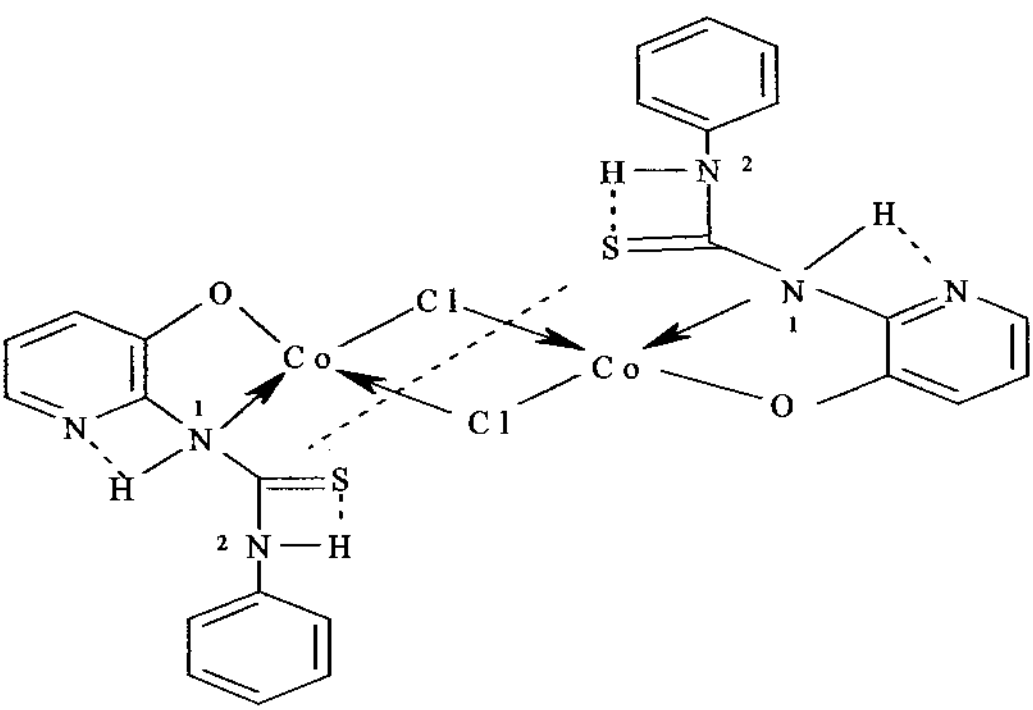


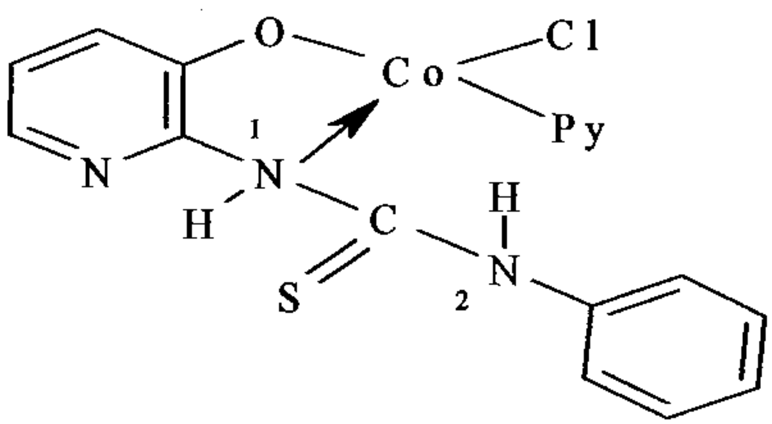
Fig. 34 . Infrared spectrum of [$Co_2(C_{12}H_{10}N_3OS)_2Cl_2$] EtOH in Nujol mull.

Also, the obscure of the strong OH band at 3520 cm^{-1} suggests the participation of this group in bonding with displacement of a hydrogen atom. All these foundations suggest that the ligand coordinates in a bidentate fashion *via* ^{1}NH and OH groups with displacement of a hydrogen atom from the latter group forming five–member ring around the Co(II) ion. Moreover, the spectrum shows four bands in the 500–200 cm^{-1} region. The bands observed at 500 and 387 cm^{-1} are assigned to υ(Co-O) and υ(Co-N) vibrations[(42-43)], respectively. The two bands located at 337 and 295 cm^{-1} are assigned to υ (Co-Cl) vibrations. The observation of those two bands for (Co-Cl) suggests that the two chloride ions are not identical and are existing in a cis-form[(47)] and represented by structure 18.



(structure 18)

The existence of chlorine bridge is confirmed by adding pyridine which destroy this bridge forming a monomeric form as shown in structure 19.



(structure 19)

The electronic spectrum of the Co(II) complex in Nujol mull (Fig. 35) shows three bands at 16051 cm^{-1} (623 nm), 16892 cm^{-1} (592 nm) and 17572 cm^{-1} (496 nm) assigned to $^4A_2 \longrightarrow {}^4T_1$ (P) transition in a tetrahedral geometry around the Co(II) ion[49,50]. The low value of magnetic moment (4.0 B.M.) is taken as additional evidence for the existence of tetrahedral structure around the Co (II) ion [50].

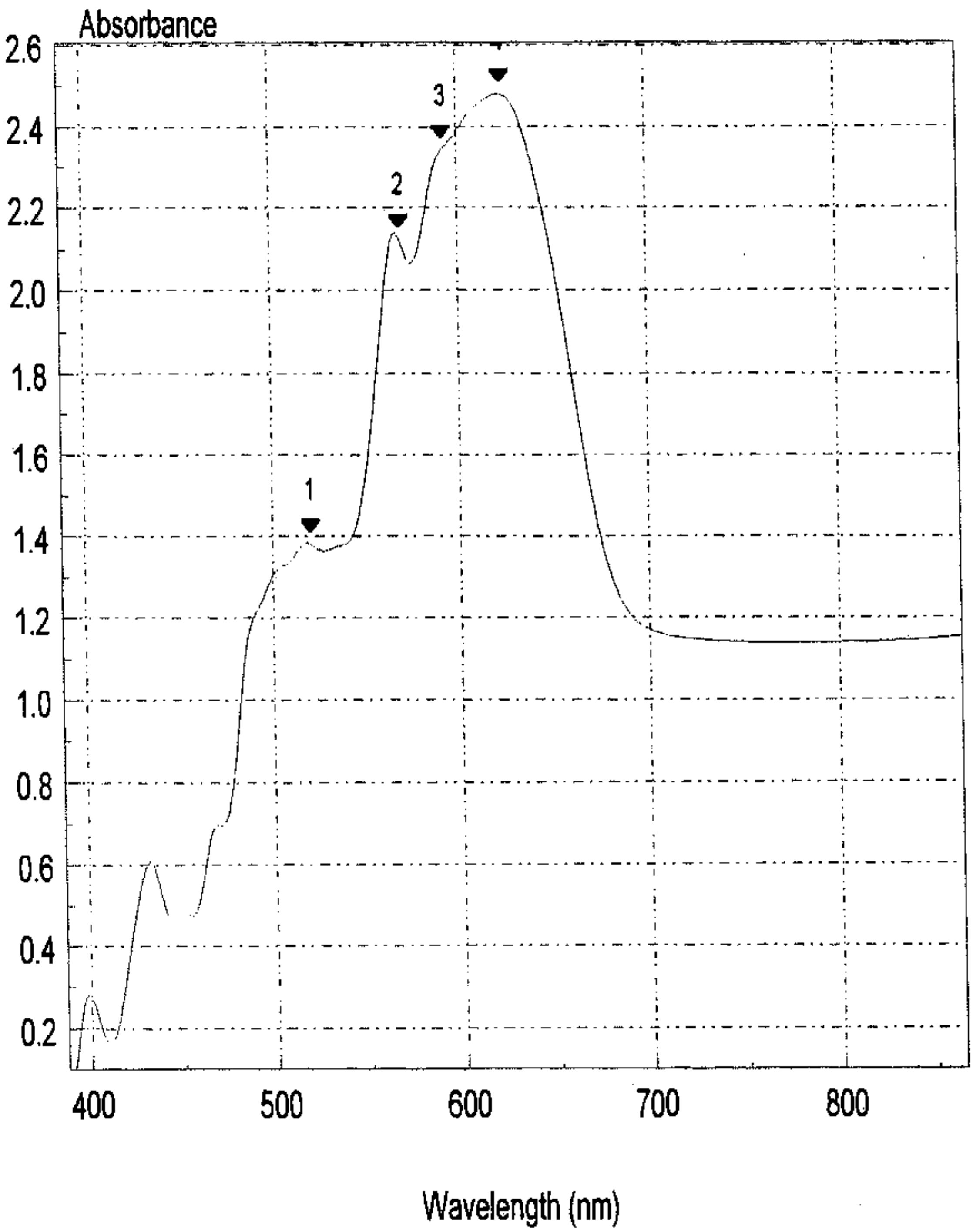
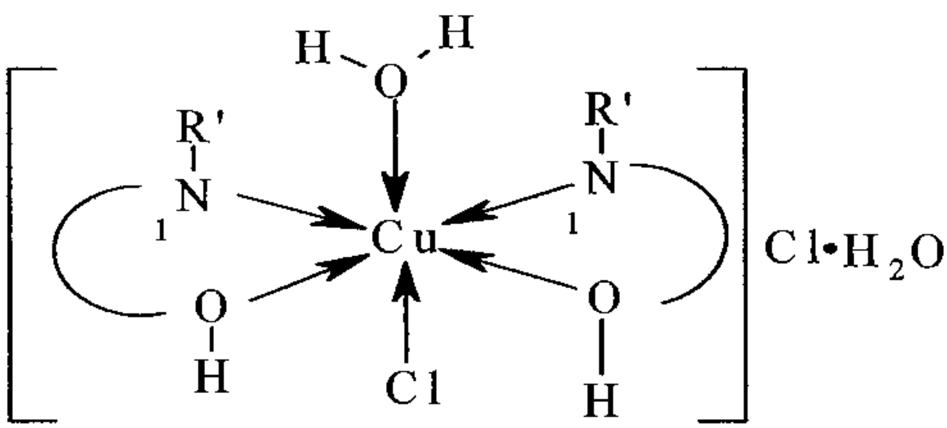


Fig. 35 . Electronic spectrum of $[Co_2(C_{12}H_{10}N_3OS)_2Cl_2]EtOH$ in Nujol mull.

The IR spectrum of the second yellowish–green Cu(II) complex, $[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.H_2O$, in Nujol mull is shown in Fig. 36. On comparing the spectra of the Cu(II) complex (Fig. 36) with HPPTU (Fig. 4), we observed that the bands due to (-N-C=S) and C=S remain existing and observed at 1569, 1494, 1459, 1260 and 750 cm^{-1} indicating that this group is not taking part in coordination. On the other hand, the bands due to the OH and ^{1}NH are shifted to lower wavenumbers and observed at 3203 and 3116 cm^{-1}, respectively. Five bands are observed at 500, 475, 314, 293 and 278 cm^{-1}. The latter band at 278 cm^{-1} is assigned to υ(Cu-Cl) vibration[42,44] while the former two bands are attributed to υ(Cu-O) vibration[42]. The two bands at 314 and 293 cm^{-1} are assigned to υ(Cu-N) vibration[43]. The observation of two bands for both Cu-O and Cu-N suggests that the ligand (HPPTU) coordinates in a cis-form as shown in structure 20.



R' = -CS-NH-Ph

(structure 20)

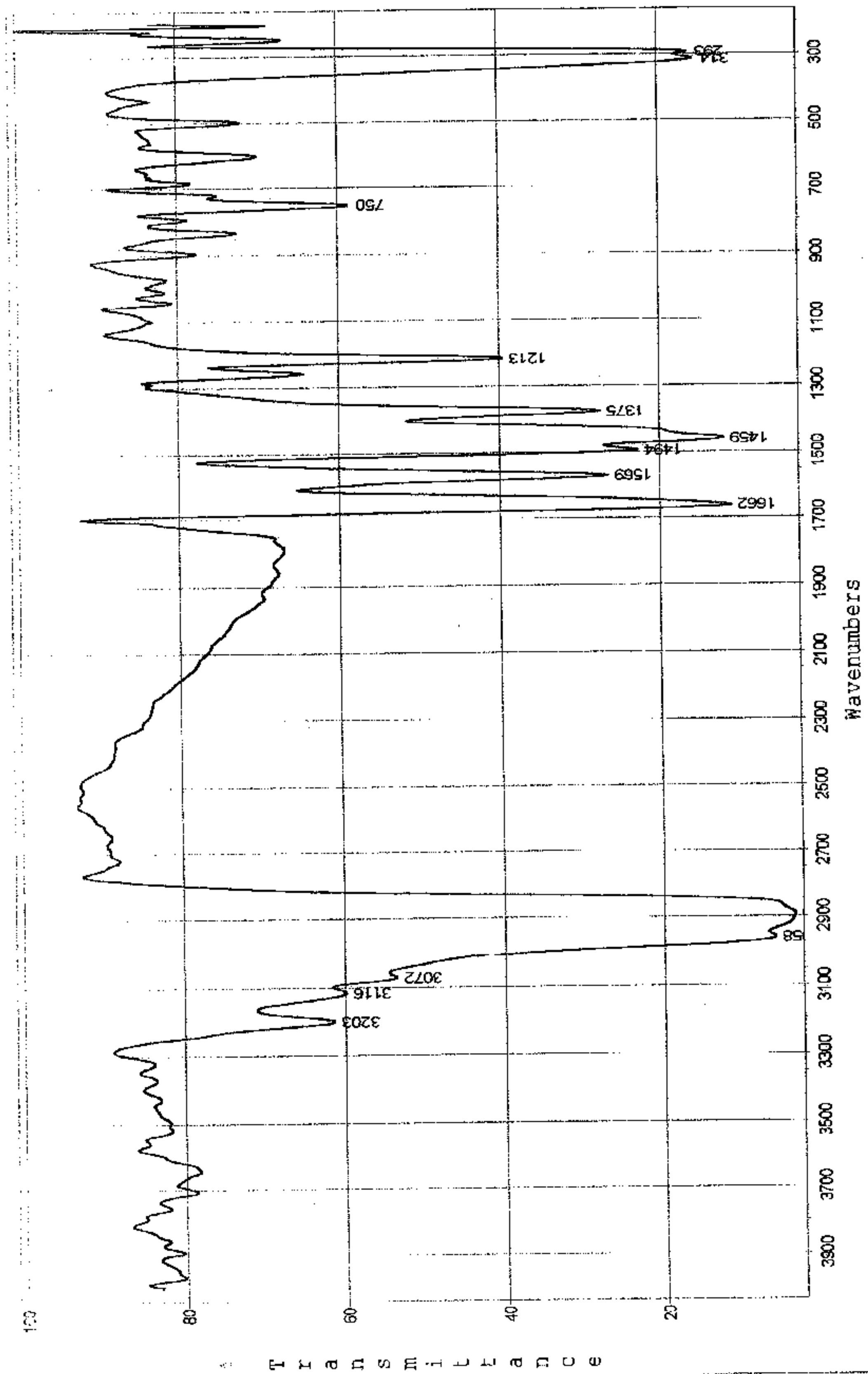


Fig. 36 . Infrared spectrum of [Cu($C_{12}H_{11}N_3OS$)$_2$Cl.H_2O]Cl. H_2O in Nujol mull.

The electronic spectrum of the Cu(II) complex in Nujol mull (Fig. 37) shows a broad band centered at 12853 cm^{-1} (778 nm). This band is attributed to $^2E_g \longrightarrow {}^2T_{2g}$ transition in a distorted-octahedral geometry around the Cu(II) ion[45]. The value of magnetic moment (2.20 B.M.) suggests the existence of monomeric form and the existence of one unpaired electron. Finally, the value of molar conductance (31.7 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a 1:1 electrolyte [41].

The IR spectrum of the yellowish–green Cu(II) complex, $[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$, is shown in Fig. 38. On comparing the IR spectra of the complex with the free ligand (Fig. 6), we observed that the bands at 1538, 1494 and 1454 cm^{-1} due to (-N-C=S)[32,33,36] in the free ligand are shifted to higher wave-numbers and are observed at 1625, 1523 and 1459 cm^{-1} in the spectrum of the Cu(II) complex. These shifts suggest that the ^{1}NH group is probably participate in bonding. Also, the negative shift of the OH band suggests the involvement of this group in bonding. On the other hand, the bands at 1267 and 754 cm^{-1} (Fig. 4) due to υ(C=S) vibration remain more or less at the same positions, in the spectrum of the Cu(II) complex, indicating that the thioketo group does not participate in bonding. Also, the bands observed at 460 and 283 cm^{-1} are assigned to υ(Cu-O)[42] and υ (Cu-Cl)[42,44] vibrations, respectively.

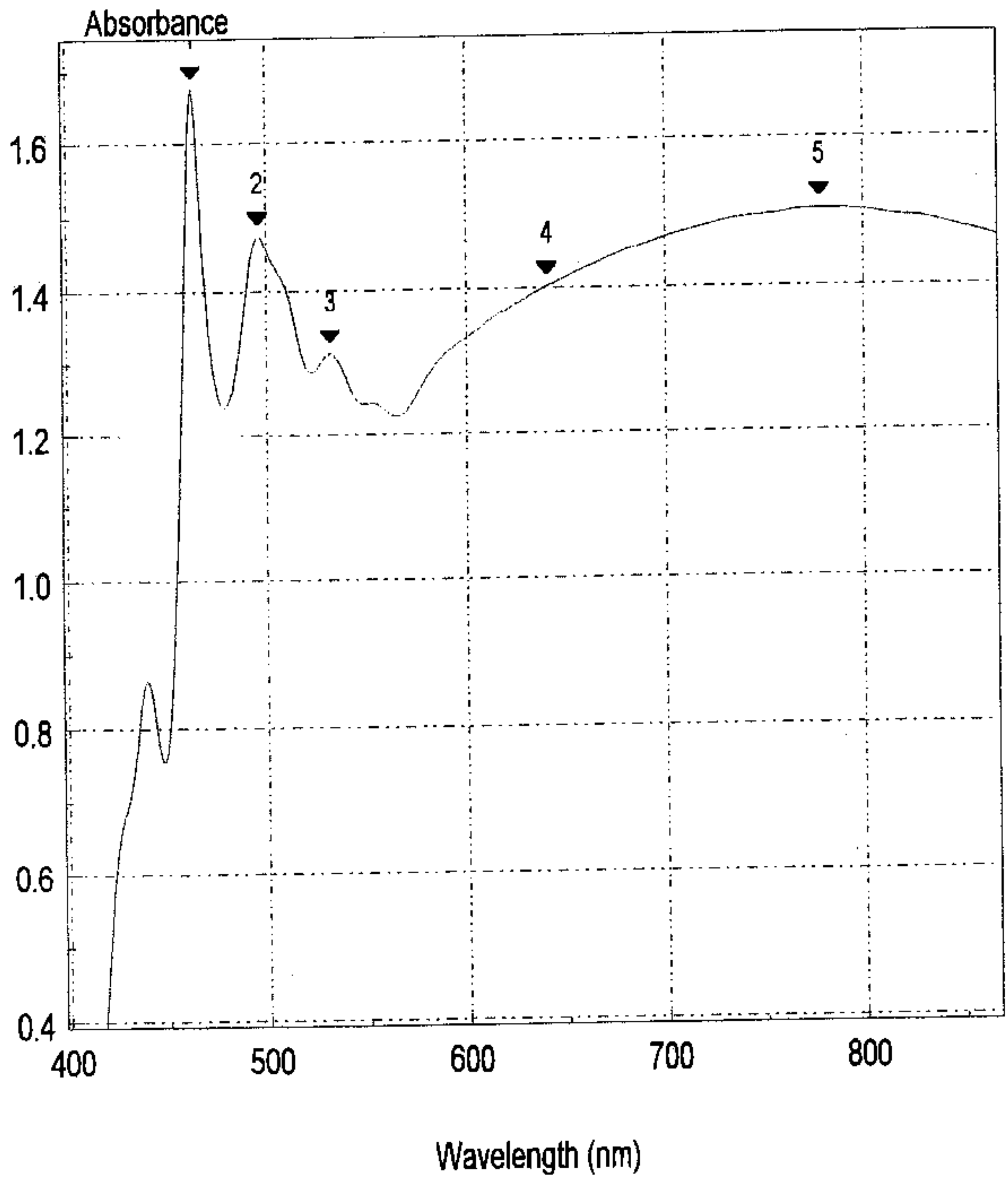


Fig. 37. Electronic spectrum of $[Cu(C_{12}H_{11}N_3OS)_2Cl.H_2O]Cl.\ H_2O$ in Nujol mull.

The electronic spectrum of the Cu(II) complex in Nujol mull (Fig. 39) shows a broad band centered at 12315 cm^{-1} (812 nm) attributed to $^2E_g \longrightarrow {}^2T_{2g}$ transition in a distorted–octahedral geometry around the Cu(II) ion(45). The value of molar conductance (66.3 $\Omega^{-1}.cm^2.mol^{-1}$.) suggests a 1:2 electrolyte(41). The low value of magnetic moment (1.23 B.M.) may suggest a partial copper-copper interaction(46). The electronic spectrum of the Cu(II) complex in Nujol mull (Fig. 37) shows a broad band centered at 12853 cm^{-1} (778 nm). This band is attributed to $^2E_g \longrightarrow {}^2T_{2g}$ transition in a distorted-octahedral geometry around the Cu(II) ion(45).

The value of magnetic moment (2.20 B.M.) of the complex, $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$ suggests the existence of monomeric form and the existence of one unpaired electron. Finally, the value of molar conductance (49.0 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a 1:1 electrolyte(41).

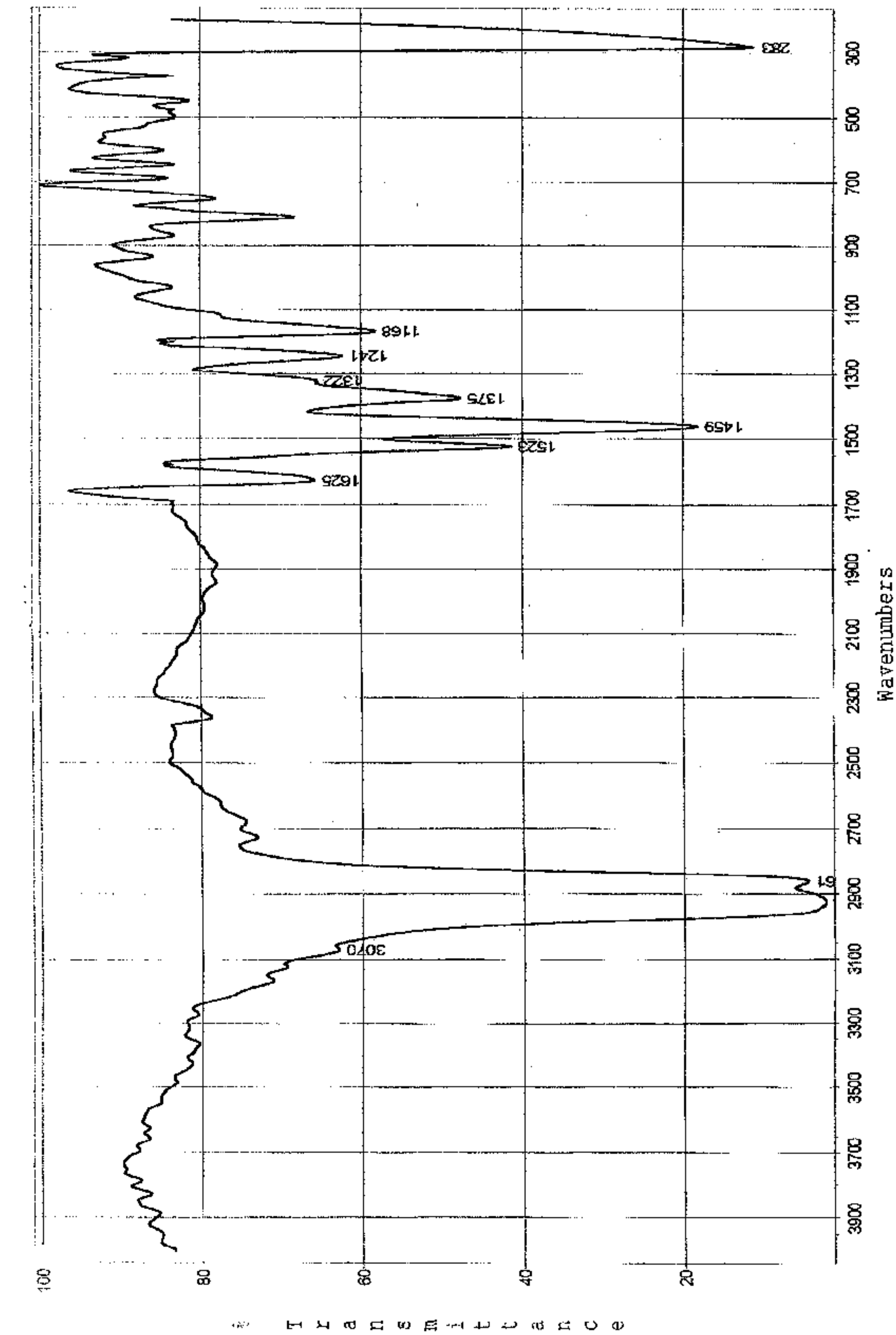
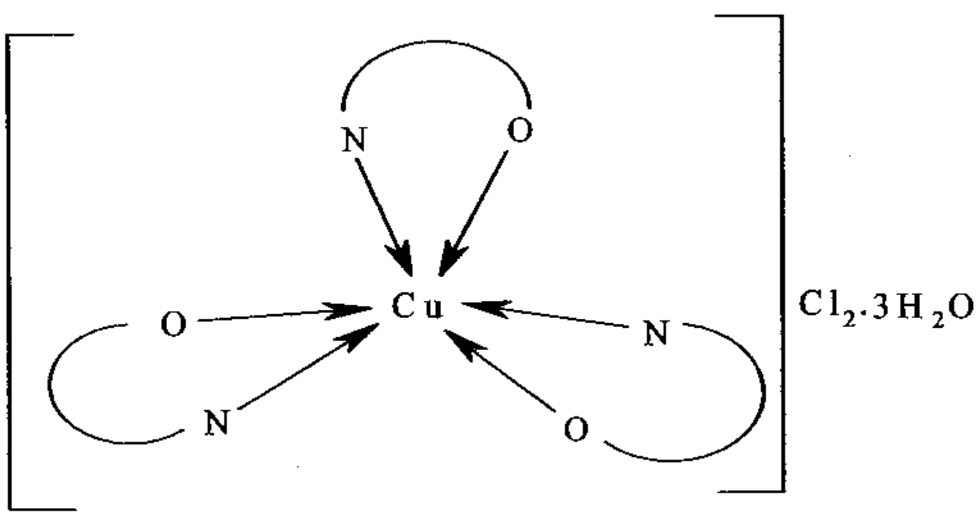


Fig. 38. Infrared spectrum of [Cu $(C_{13}H_{12}N_2OS)_3$Cl.H_2O]Cl_2. $3H_2O$ in Nujol mull.

All these foundations suggest that the free ligand coordinates in a bidentate manner *via* the ^{1}NH and OH groups forming a five–member ring around the Cu(II) ion (structure 21).



(structure 21)

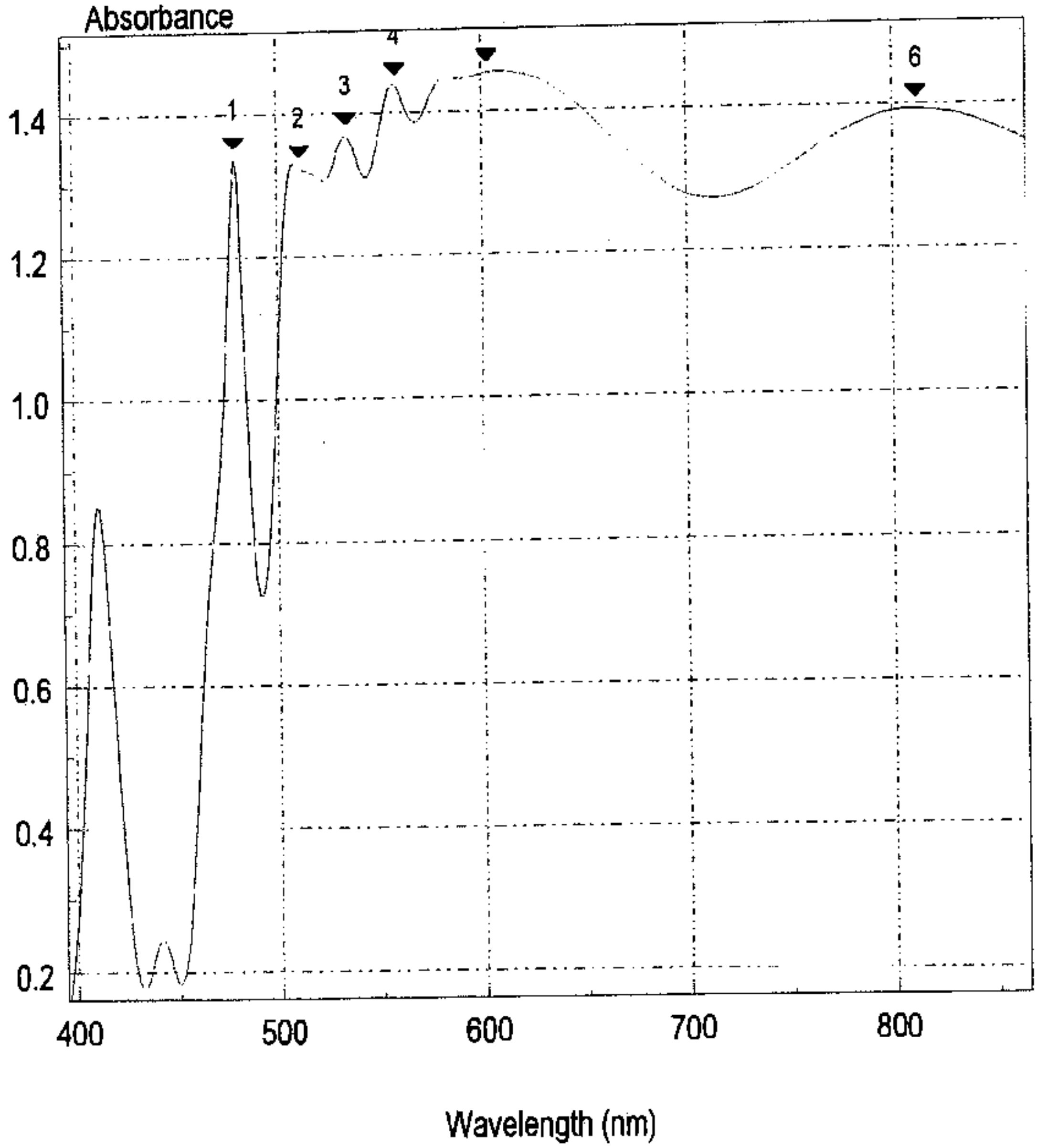


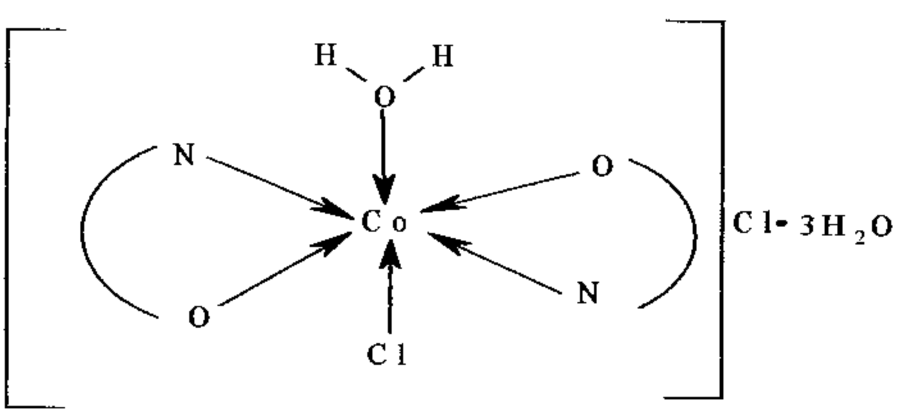
Fig. 39. Electronic spectrum of $[Cu(C_{13}H_{12}N_2OS)_3]Cl_2.3H_2O$ in Nujol mull.

Finally, the IR spectrum of the brown Co(II) complex, $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$, in Nujol mull (Fig. 40) is similar to a great extent to the IR spectrum of the Cu(II) complex (Fig. 38). This suggests that the ligand coordinates in a bidentate manner *via* the NH and OH groups forming a five-member ring around the Co(II) ion. Also, the spectrum shows three weak bands at 475, 314 and 285 cm^{-1} assignable to υ(Co-O)[42], υ(Co-Cl)[(44)] and υ(Co-N)[(43)] vibrations , respectively .

The electronic spectrum of the cobalt complex in DMF (Fig. 41) shows two bands at 18797 cm^{-1} (532 nm) and 17483 cm^{-1} (637 nm) assigned to $^4T_{1g} \longrightarrow {}^4A_{2g}$ and $^4T_{1g} \longrightarrow {}^4T_{1g}$ (p) transitions in an octahedral geometry around the Co(II) ion[(52)].

The value of magnetic moment (5.11 B.M.) is taken as an additional evidence for the octahedral geometry around the Co(II) ion. The molar conductance (49 $\Omega^{-1}.cm^2.mol^{-1}$) suggests the existence of 1:1 electrolyte [(41)].

All these foundations suggest structure 22 for the Co(II) complex.



(structure 22)

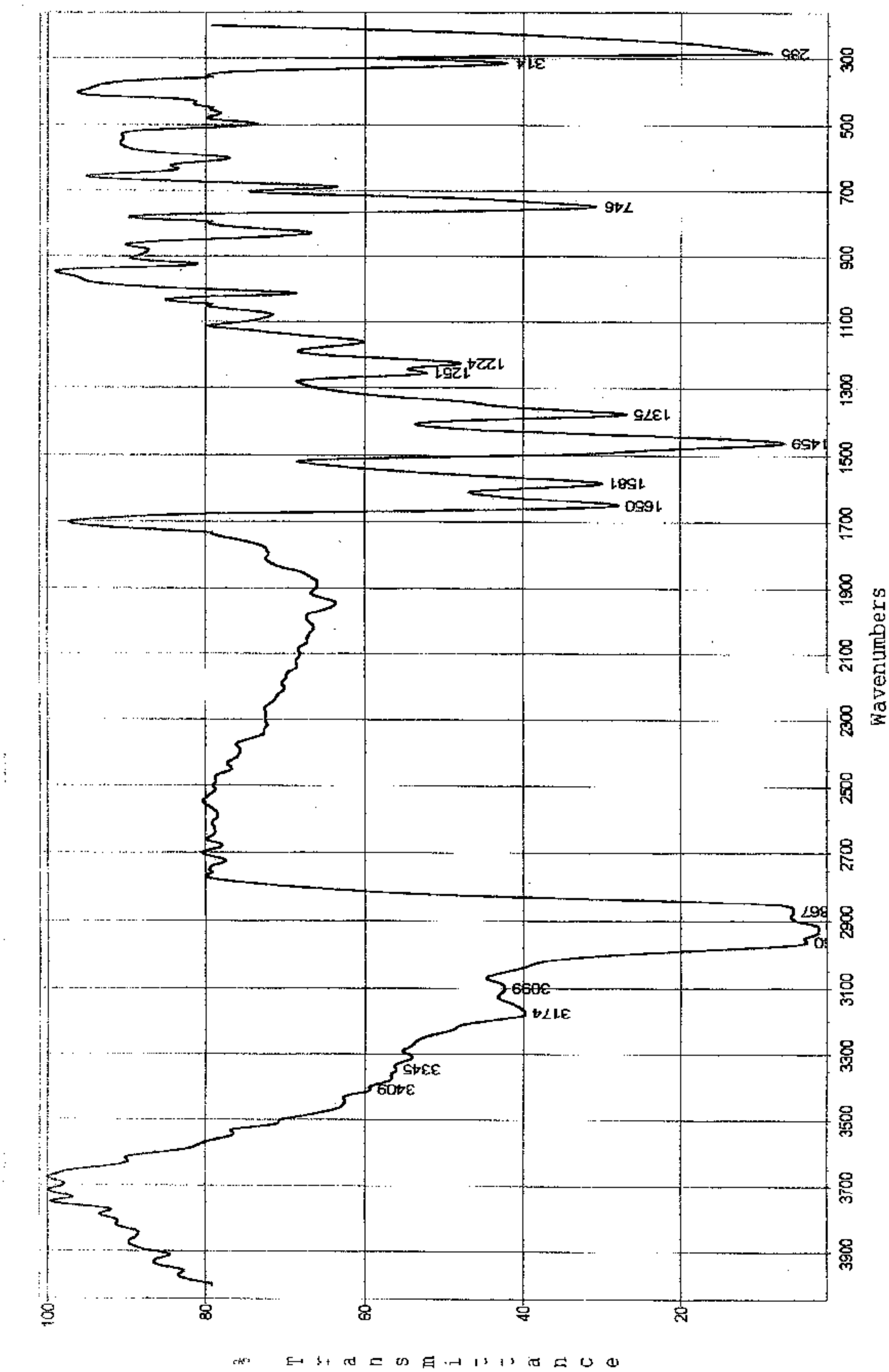


Fig. 40. Infrared spectrum of $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$ in Nujol mull.

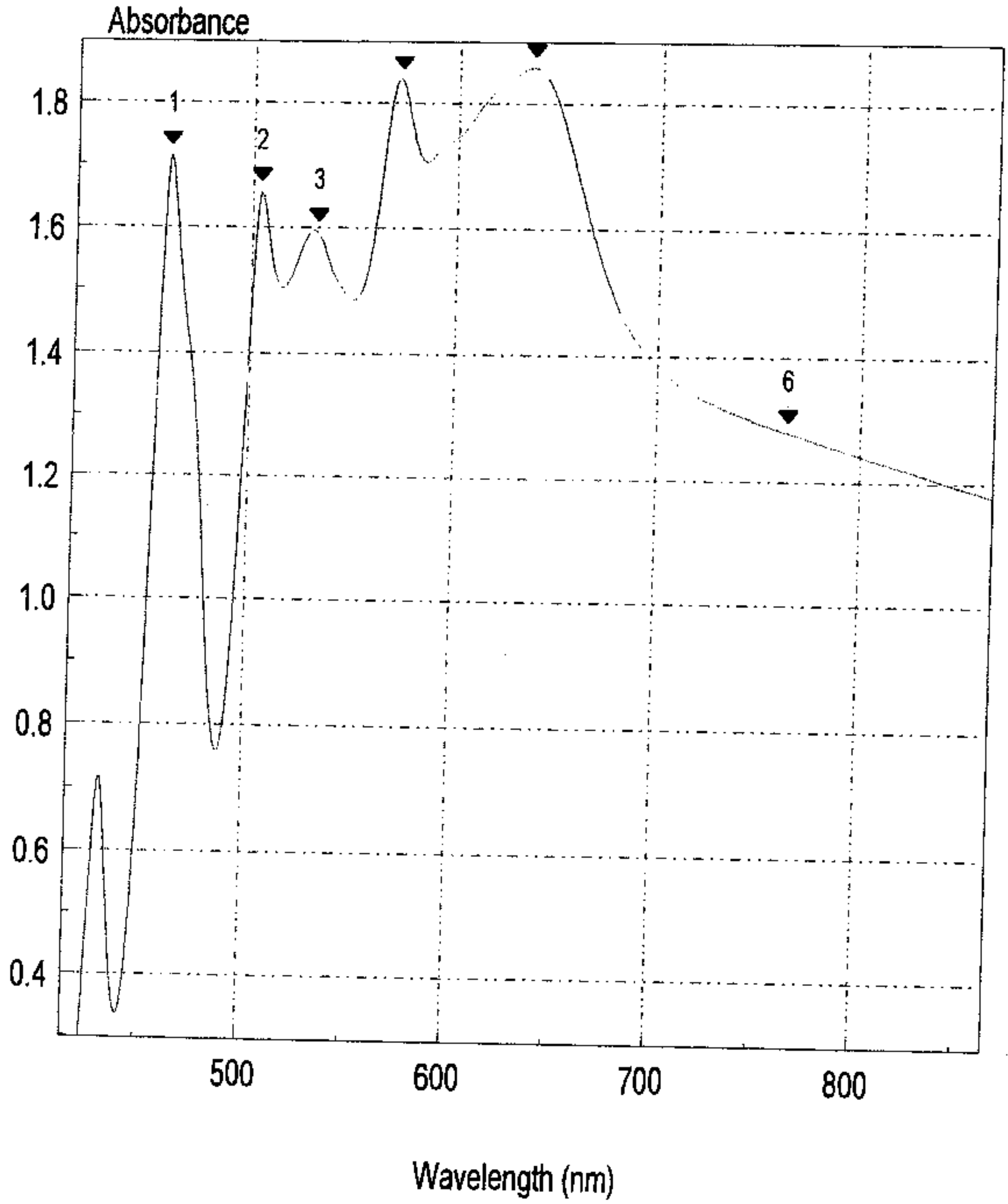


Fig. 41. Electronic spectrum of $[Co(C_{13}H_{12}N_2OS)_2Cl.H_2O]Cl.H_2O$ in Nujol mull.

4.4. Spectral, Conductance and Magnetic Moments for the Cu(II) and Co(II) Complexes Derived from ATHTC, ETHTC and PTHPC.

Five different Co(II) and Cu(II) complex with the general formulae, $[Co(C_9H_{19}N_4OS)_2]Cl_4.4H_2O$, $[Co(C_9H_{19}N_4OS)Cl_2]Cl$, $[Co(C_8H_{18}N_4OS)Cl_2]Cl.2H_2O.1/2EtOH$, $[Co(C_{14}H_{15}N_4OS)Cl_2]Cl.2 EtOH$ and $[Cu(C_{14}H_{15}N_4OS)Cl_2.H_2O]Cl.1/2EtOH$, have been isolated and characterized.

The values of magnetic moments for the former two Co(II) complexes, $[Co(C_9H_{19}N_2OS)_2]Cl_2.4H_2O$ and $[Co(C_9H_{19}N_2OS)Cl_2]Cl$, are 4.5 and 4.3 B.M., respectively, indicating a tetrahedral geometry around the Co(II) ion. Also, the blue colours of those two complexes are taken as an additional evidence for the existence of tetrahedral geometry around the Co(II) ion in those two complexes. On the other hand, the values of molar conductance of those two complexes in DMF are 145.5 and 38.6 $\Omega^{-1}.cm^2.mol^{-1}$ suggesting a 1:4 electrolyte for the former Co(II) complex, while 1:1 electrolyte for the latter Co(II) complex. The IR spectra of those two complexes are more or less the same. The IR spectrum of the former complex, $[Co(C_9H_{19}N_4OS)_2]Cl_4.4H_2O$, in Nujol is shown in Fig. 42. The spectrum shows a positive shift of the carbonyl oxygen band to higher wavenumber (1725 cm^{-1}), while the bands due to the thioketo group remain unchanged and appear at 540, 1479 and 1413 cm^{-1}. The band observed at 1581 cm^{-1} is assigned to-$CH=CH_2$ group. Also, the IR spectrum shows four bands, in the 500 - 200 cm^{-1} region, at 475, 460, 327 and 285 cm^{-1}.

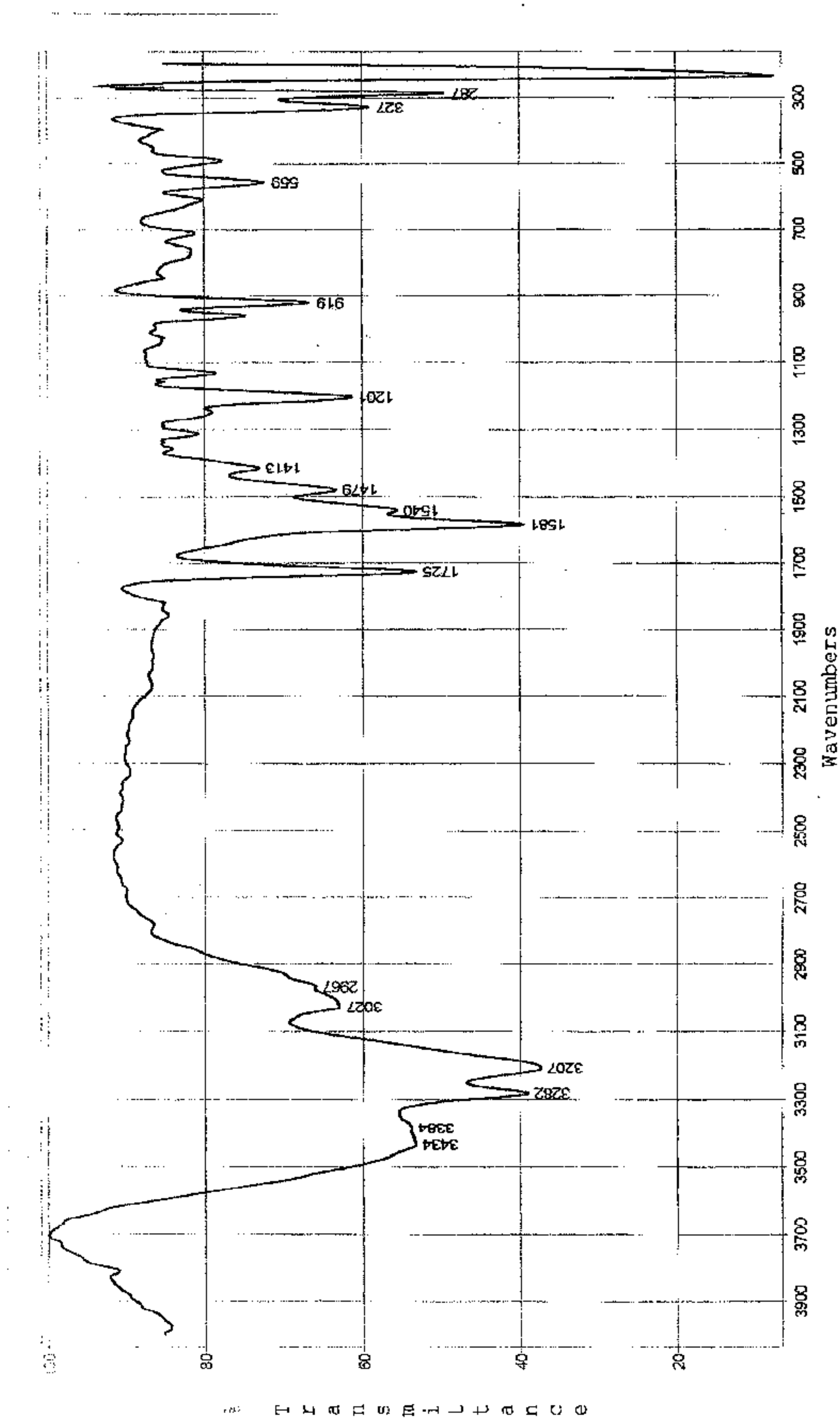
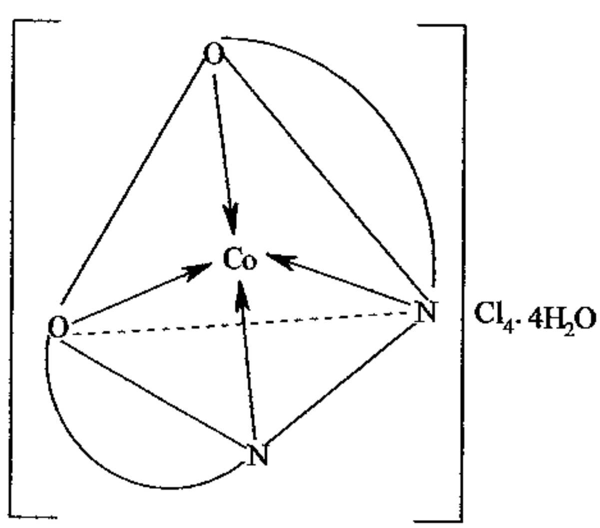


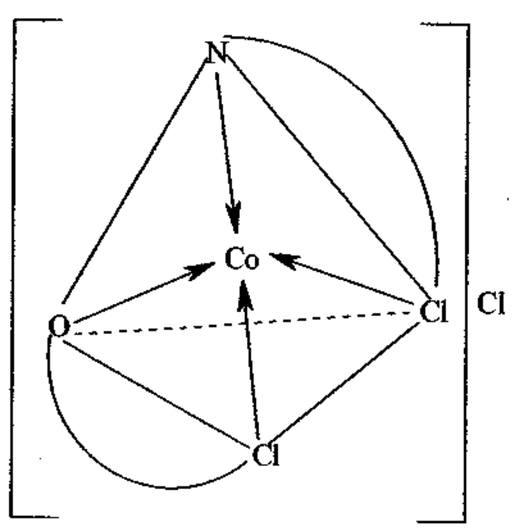
Fig. 42. Infrared spectrum of [$Co(C_9H_{19}N_4OS)_2$]$Cl_4.4H_2O$ in Nujol mull.

The first two bands are assigned to υ(Co-O) vibration[42-44], while the latter two bands are assigned to υ(Co-N) vibration[43]. The observation of two bands for each suggests that the ligand (ATHTC) coordinates to the Co(II) ion the a bidentate manner *via* the NH and CO groups forming a five - member ring around the Co(II) ion. Also, the existence of two bands for each (Co-N)[43] and (Co-O)[42] suggests that the ligand coordinates in a cis-position.

The electronic spectra of the former two complexes (Figs. 34 and 44) in Nujol mull show three bands for each at 13550 cm^{-1} (738 nm), 15314 cm^{-1} (653 nm) and 16155 cm^{-1} (619 nm) for the former complex while at 14472 (691 cm^{-1}) (688 nm), 14970 cm^{-1} (691 nm) and 15773 cm^{-1} (634 nm) for the latter complex. These three bands are assigned to $^4A_2 \longrightarrow {}^4T_1$ (p) transitions in a tetrahedral geometry around the Co(II) ion[49,50]. The data suggest structures 23 and 24 for the two Co(II) complexes, respectively



(structure 23)



(structure 24)

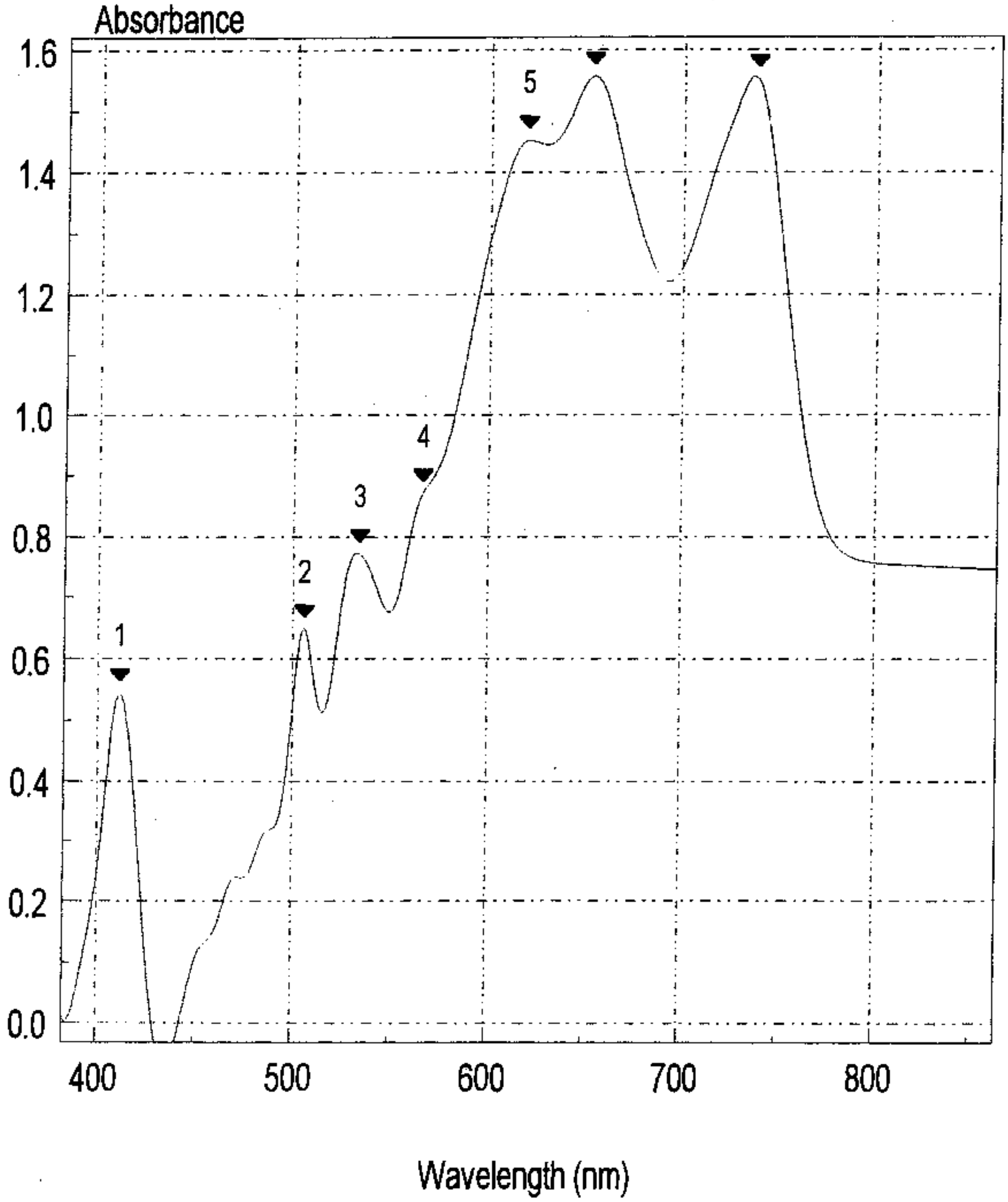


Fig. 43. Electronic spectrum of $[Co(C_9H_{19}N_4OS)_2]Cl_4.4H_2O$ in Nujol mull.

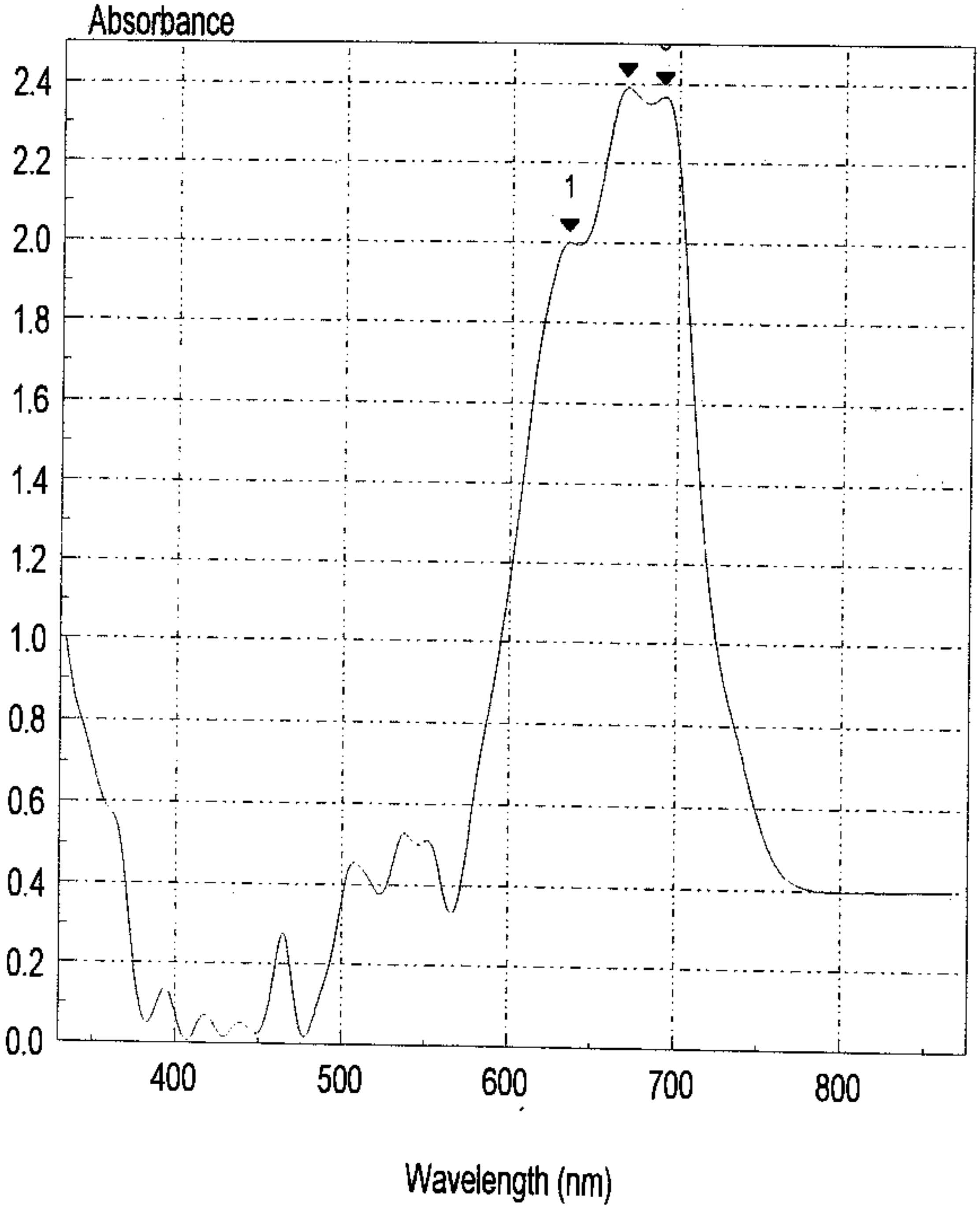


Fig. 44. Electronic spectrum of $[Co(C_9H_{19}N_4OS)Cl_2]Cl$ in Nujol mull.

The value of magnetic moment of the blue Co(II) complexes, $[Co(C_8H_{18}N_4OS)Cl]Cl.2H_2O.1/2EtOH$, is 4.50 B.M., suggests a tetrahedral structure around the Co(II) ion[(50)]. Also, the value of molar conductance in DMF (40.1 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a 1:1 electrolyte[(41)].

The electronic spectrum of this complex in Nujol mull (Fig. 45) shows three bands at 13086 cm^{-1} (715 nm), 15244 cm^{-1} (656 nm) and 16103 cm^{-1} (621 nm) assignable to $^4A_2 \longrightarrow {}^4T_1$ (p) transitions in a tetrahedral geometry around the Co(II) ion[(49,50)]. The IR spectrum of the Co(II) complex in Nujol mull (Fig. 46) shows the positive shift of the carbonyl oxygen band to higher wavenumber (1720 cm^{-1}) together with the obscure of the bands due to the thioketo group together with the appearance of a new band due to the thioenolization process with the formation of a new group (=C-SH) which is deprotonated during complex formation. The observation of new band at 634 cm^{-1} assigned to υ(C-S)[(53)] is taken as an evidence for the deprotonation of the thioenol group.

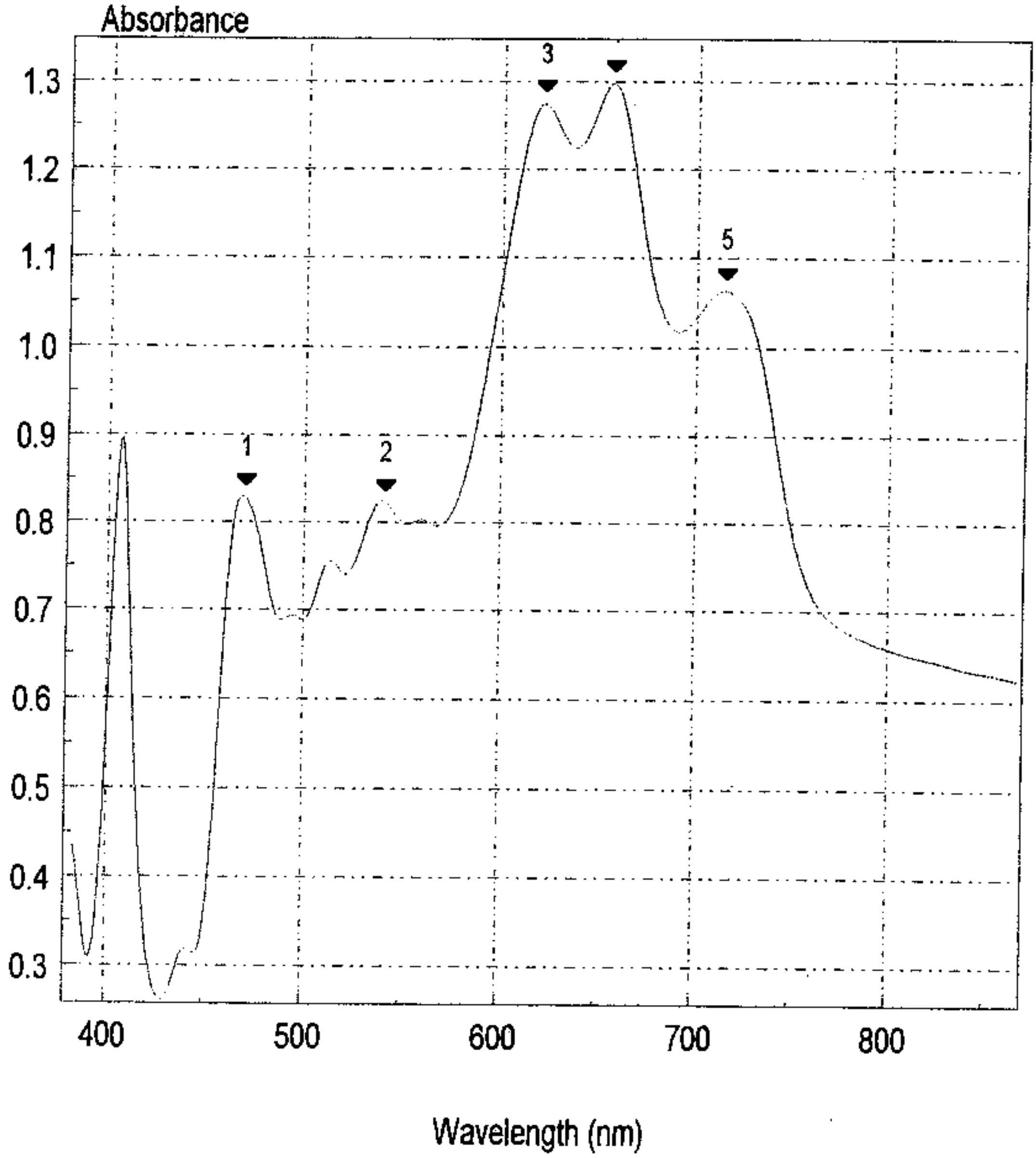


Fig. 45. Electronic spectrum of $[Co(C_8H_{18}N_4OS)Cl]Cl.2H_2O.1/2$ EtOH in Nujol mull.

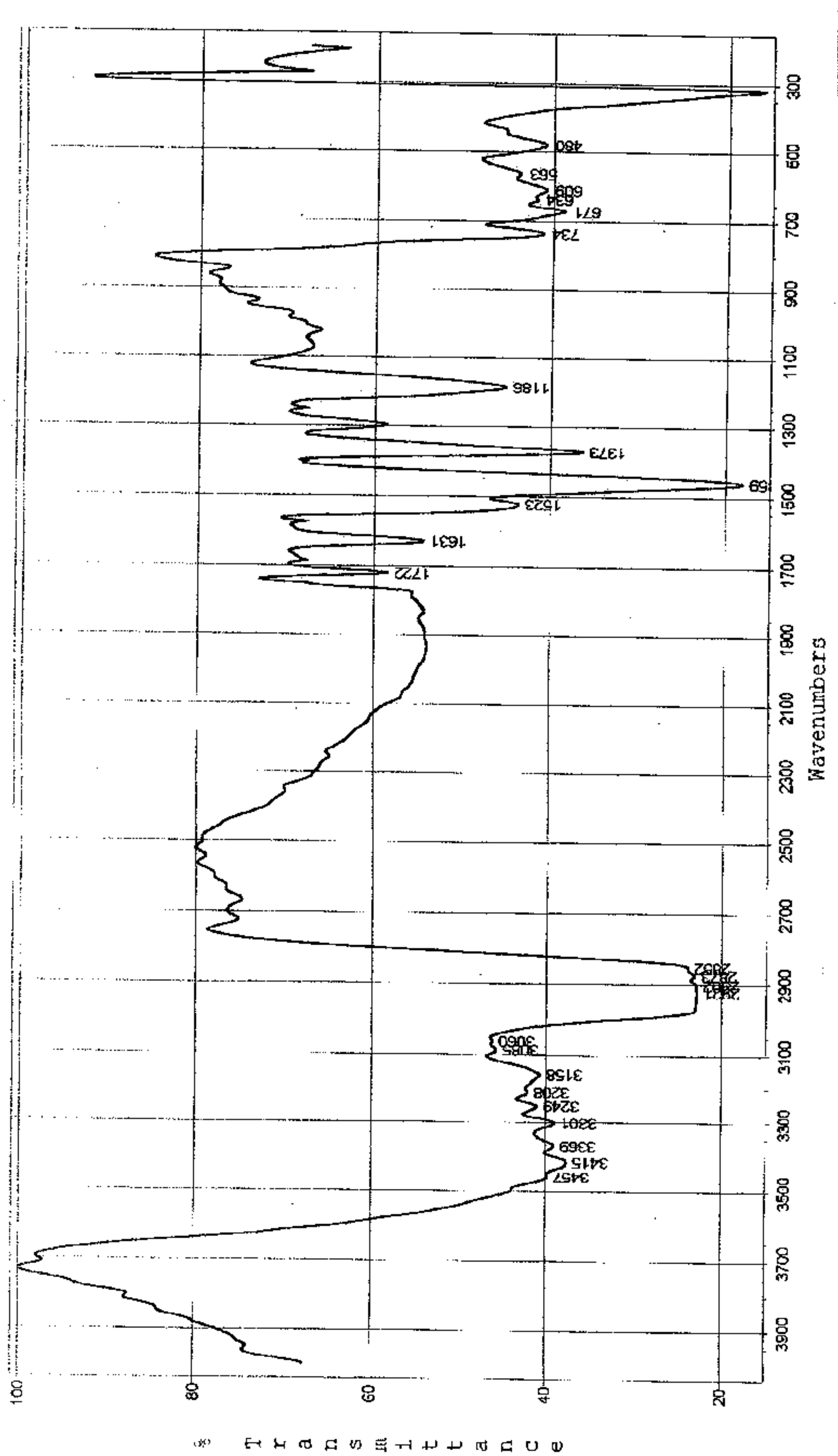
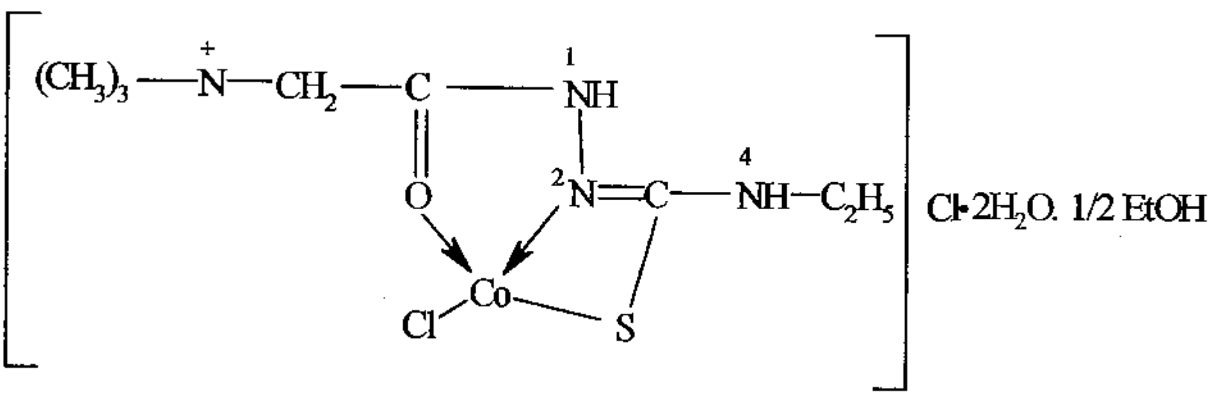


Fig. 46. Infrared spectrum of $[Co(C_8H_{18}N_4OS)Cl]Cl.2H_2O.$ 1/2EtOH in Nujol mull.

Moreover, the appearance of a new band at 1680 cm^{-1} assigned to υ(C=N) vibration is taken as additional evidence for the deprotonation of the thioenol group during complex formation. New bands are observed at 563, 480, 320 and 283 cm^{-1} assignable to υ(Co-O)[42,44], υ(Co-S), υ(Co-N)[43] and υ(Co-Cl)[44] vibrations, respectively. All these foundations suggests structure 25 for this complex.



(structure 25)

The value of magnetic moment of the petrol Co(II) complex, $[Co(C_{14}H_{15}N_4OS)Cl_2]Cl.2EtOH$, was found to be 4.04 B.M. This value suggests the existence of a tetrahedral structure around the Co(II) ion. Also, the molar conductance value in DMF (40.4 $\Omega^{-1}.cm^{-2}.mol^{-1}$) suggests a 1:1 electrolyte [41].

The electronic spectrum of the Co(II) complex in Nujol mull (Fig. 47) shows three bands at 14225 cm^{-1} (703 nm), 15015 cm^{-1} (666 nm) and 15974 cm^{-1} (626 nm). These bands are assigned to $^4A_2 \longrightarrow {}^4T_1$ (P) transitions in a tetrahedral geometry around the Co(II) ion [49,50].

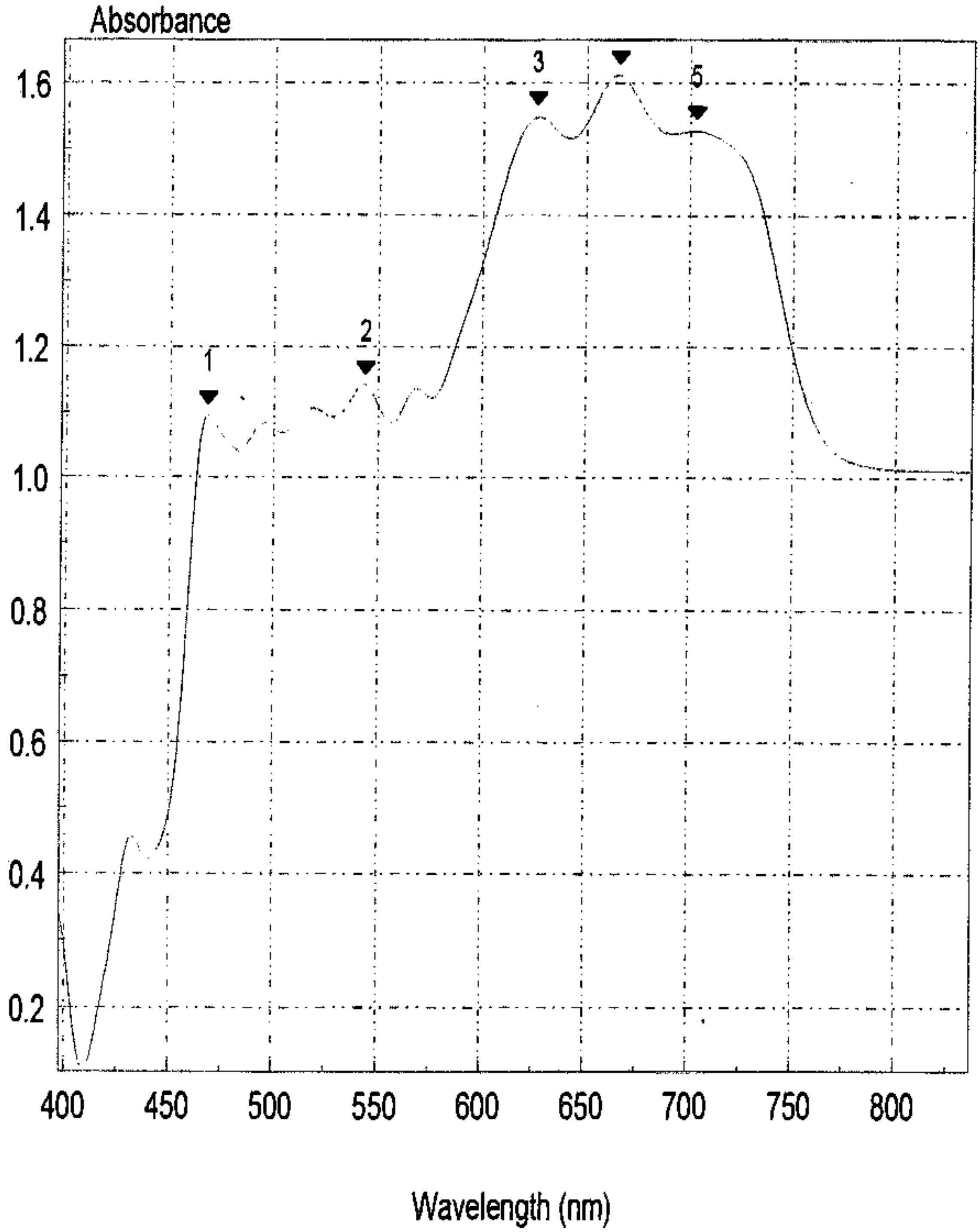
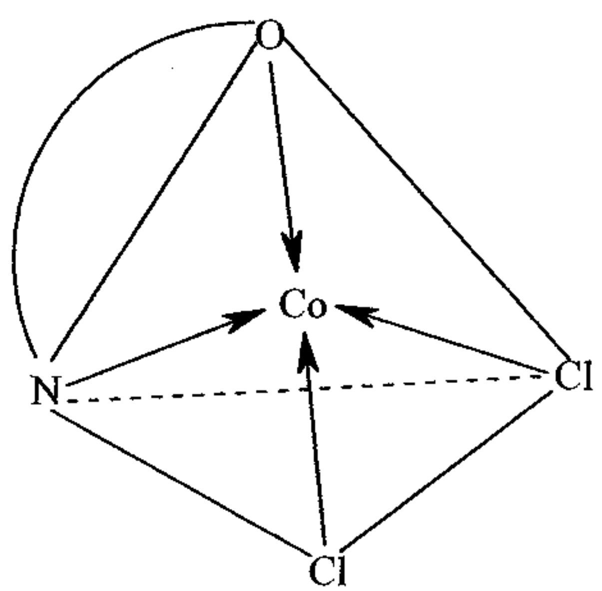


Fig. 47. Electronic spectrum of $[Co(C_{14}H_{15}N_4OS)Cl_2]Cl.2EtOH$ in Nujol mull.

The IR spectrum of the Co(II) complex in Nujol mull (Fig. 48) shows the negative shift of the band due to NH(2) together with the positive shift of the band due to the carbonyl oxygen to higher wavenumber. This suggests that the ligand (PTHPC) coordinates in a bidentate manner *via* the carbonyl oxygen and the NH(2) groups forming a five-member ring around the Co(II) ion. The IR spectrum shows also that the positions of the (-N-C=S) and CS groups remain unchanged. Moreover, the three bands at 480, 318 and 293 cm^{-1} are assigned to υ(Co-O)[42], υ(Co-N)[43] and υ(Co-Cl)[44] vibrations, respectively. All these foundations suggest structure 26 for this complex.



(structure 26)

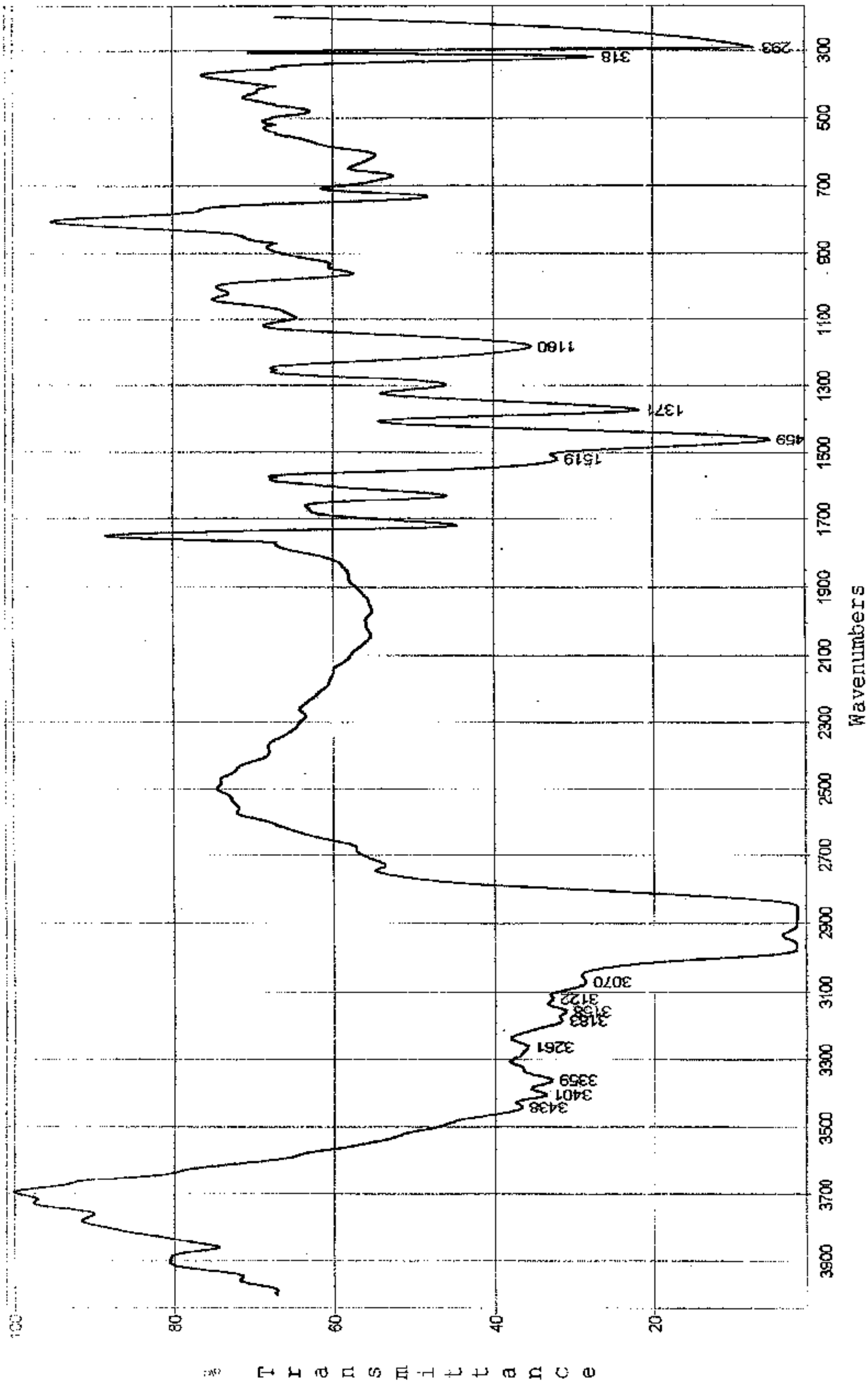
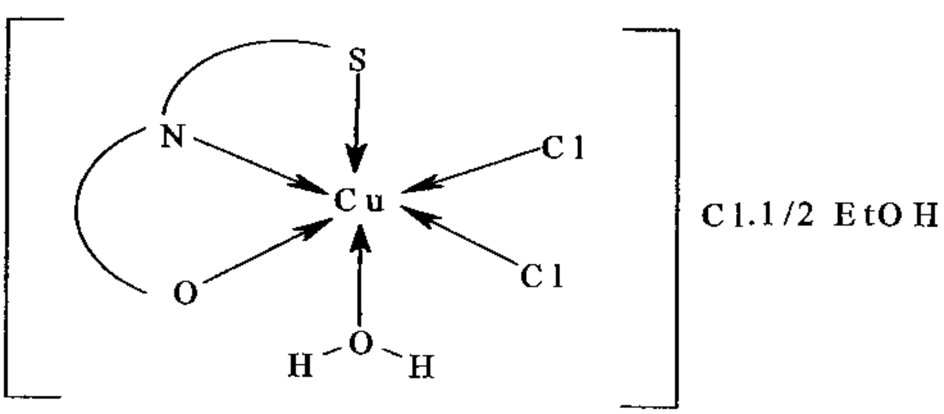


Fig. 48. Infrared spectrum of [Co($C_{14}H_{15}N_4OS$)Cl_2]Cl.2 EtOH in Nujol mull.

Finally, the value of the magnetic moment for the deep green Cu(II) complex, $[Cu(C_{14}H_{15}N_4OS)Cl_2.H_2O]Cl.1/2EtOH$, was found to be 1.89 B.M. This value suggests the existence of a monomeric structure and the absence of any copper–copper interaction[46]. The value of molar conductance in DMF (38.1 $\Omega^{-1}.cm^2.mol^{-1}$) suggests the presence of 1:1 electrolyte[41]. The electronic spectrum of the Cu(II) complex in Nujol mull, (Fig. 49) shows a broad band centered at 14368 cm^{-1} (696 nm) attributable to $^2E_g \longrightarrow {}^2T_{2g}$ transition in a distorted-octahedral geometry around the Cu(II) ion[45].

The infrared spectrum of the Cu(II) complex in Nujol mull (Fig. 50) shows that the ligand (PTHPC) coordinates in a tridentate manner *via* the carbonyl oxygen, NH(2) and the thioketo groups. The negative shifts of all these bands to lower wavenumbers and are observed at 1662, 3189 and 723 cm^{-1}. The bands observed at 507, 460, 289, 256 and 212 cm^{-1} are assigned to υ(Cu-O)[42], υ(Cu-S)[42], υ(Cu-N) and υ(Cu-Cl) vibrations, respectively. The observation of two bands for Cu-Cl suggests that those two bands are existed in a cis-position. All these foundations suggest structure 27 for this complex. .



(structure 27)

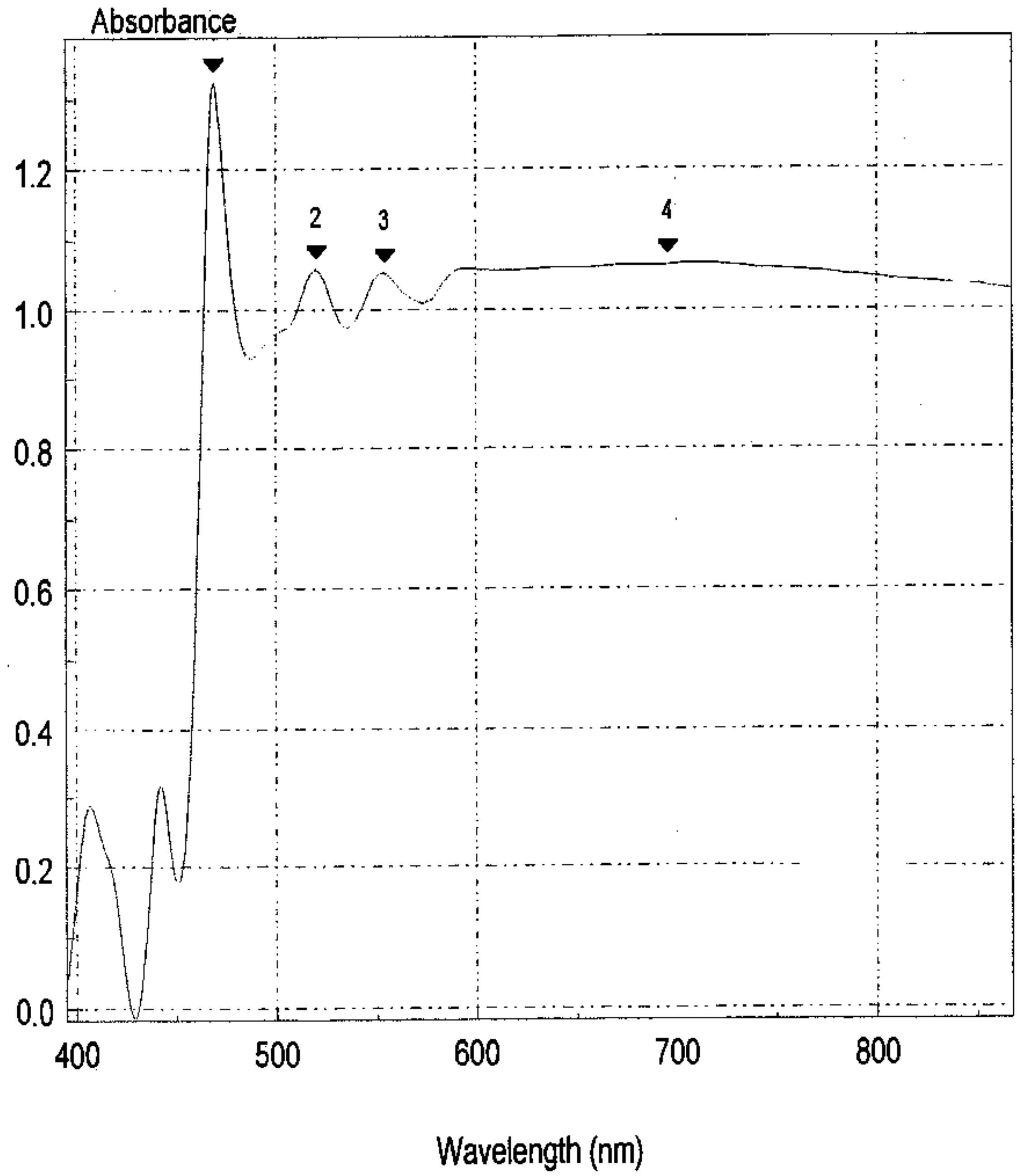


Fig. 49. Electronic spectrum of [Cu($C_{14}H_{15}N_4OS$)Cl_2.H_2O]Cl.1/2EtOH in Nujol mull.

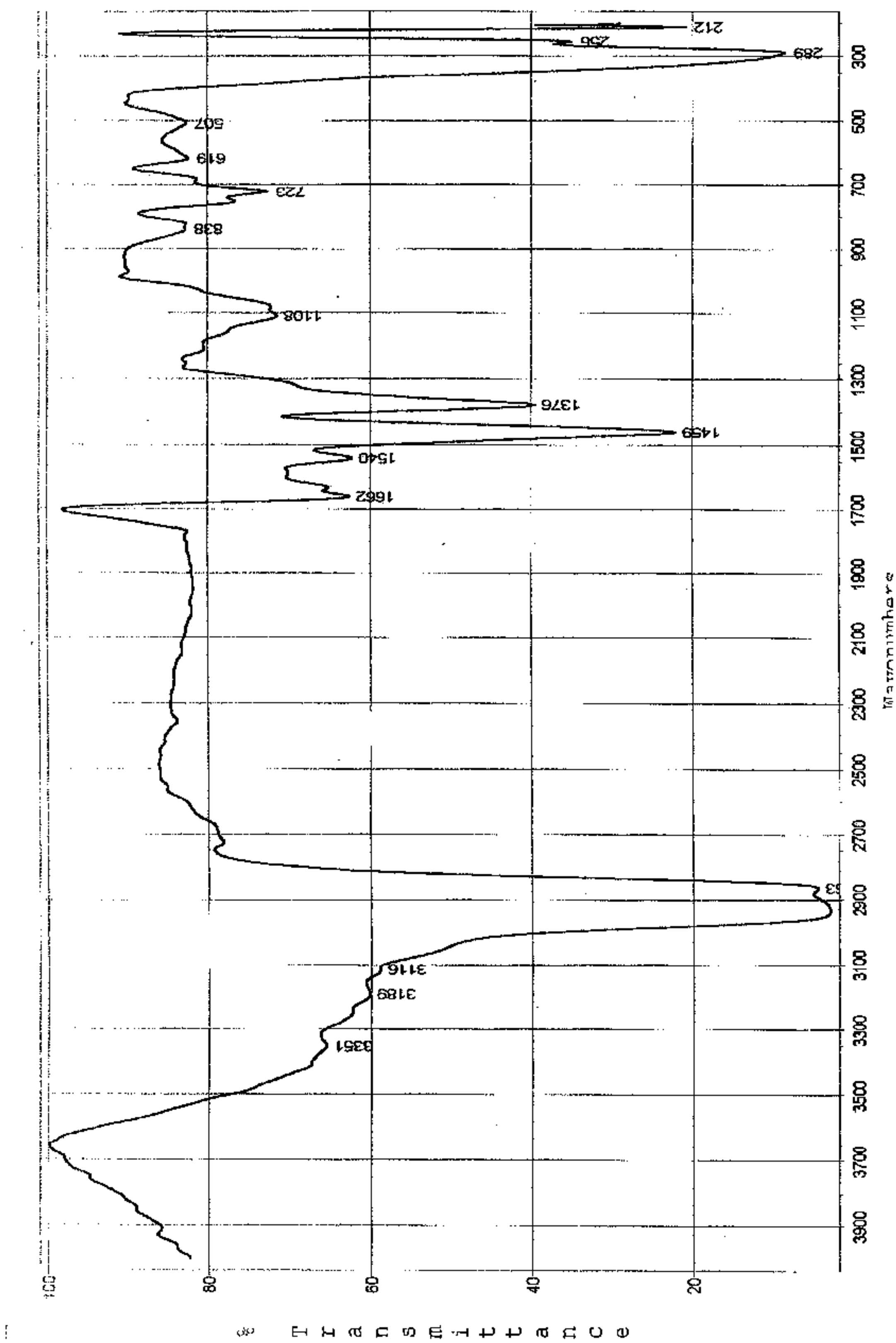


Fig. 50. Infrared spectrum of [Cu($C_{14}H_{15}N_4OS$)Cl_2.H_2O]Cl.1/2EtOH in Nujol mull.

5. Characterization of the Solid Metal Complexes Derived by Tribochemical Reaction Method.

5.1. Spectral, Conductance and Magnetic Moments for the Complexes Derived From G.P.

Three novel complexes have been prepared by tribochemical reactions having the general formulae, $[Co(C_7H_{10}N_3O)I_2.1/2EtOH.1/2H_2O]I.H_2O$, $[Cu(C_7H_{10}N_3O)I_2][Cu\ I_2.1/2EtOH\ ]2H_2O$ and $[Cu(C_7H_{10}N_3O)I_2][Cu\ I_3.1/2\ EtOH]$.

The value of molar conductance for the first selmon complex (30.8 $\Omega^{-1}.cm^2.mol^{-1}$) suggests the electrolytic nature of this complex (1:1)[41]. Also, the colour of this complex changes to yellow on long standing (two months) at room temperature (25 °C). The low value of magnetic moment for the yellow complex is 1.7 B.M. This value suggests that the complex may have a low–spin octahedral structure around the Co(II) ion [56,57].

The IR spectrum of the Co(II) complex in KBr (Fig. 51) is compared with the spectra of the free ligand (Fig. 1) and the Co(II) complex derived by conventional chemical method (Fig. 29). The spectrum (Fig. 51) shows that the ligand (G.P.) coordinates in a bidentate manner *via* the carbonyl oxygen and NH_2 groups forming five–member ring around the Co(II) ion. The negative shifts of those two bands to lower wavenumbers are taken as evidence for the participation of those groups in bonding. Those two bands are observed as a strong bands at 1658 cm^{-1} and a shoulder at 1620 cm^{-1}. Also, the two bands observed at 482 and 285 cm^{-1} are assigned to υ(Co-O) and υ(Co-N) vibrations[42,43], respectively.

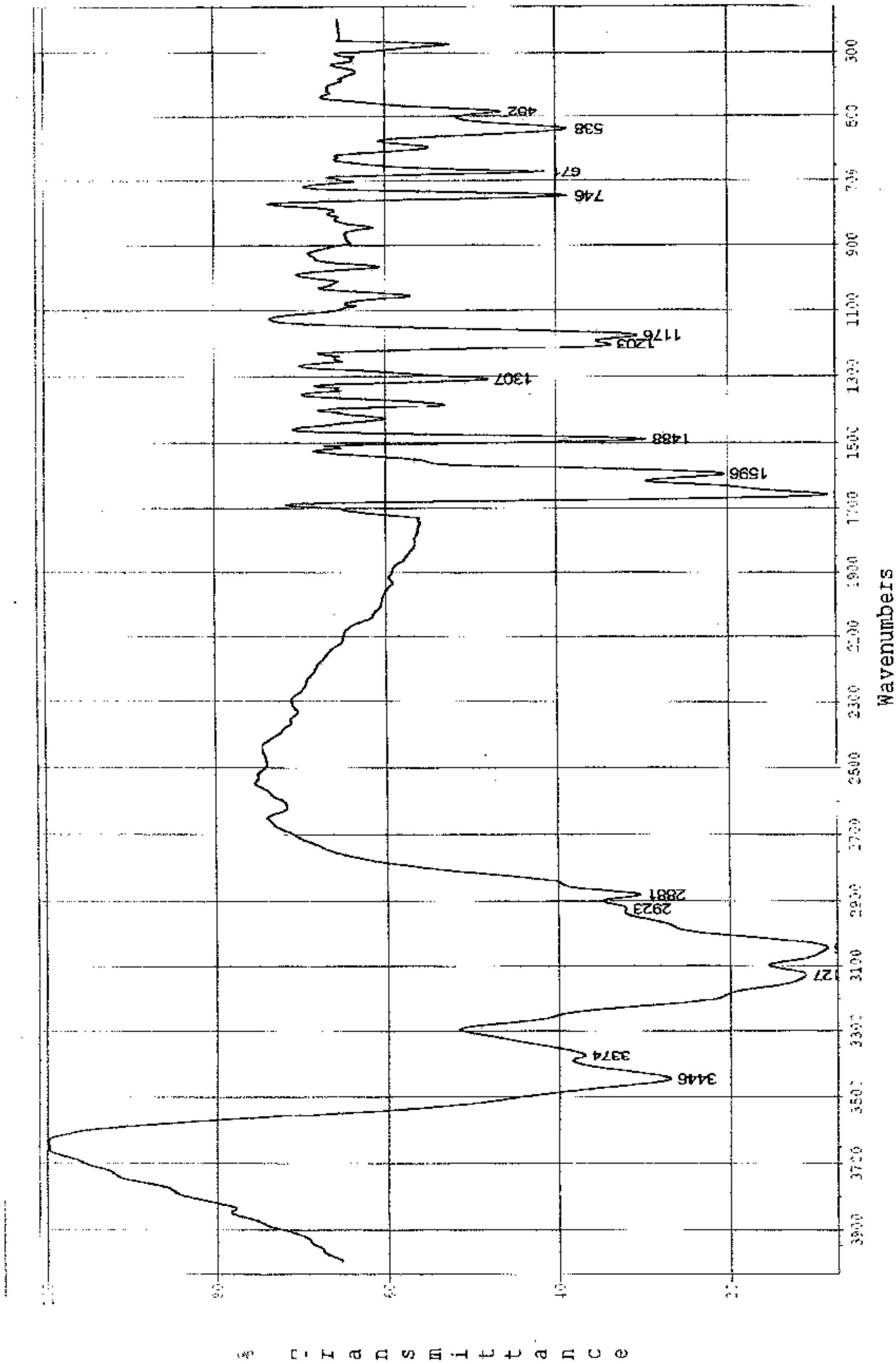
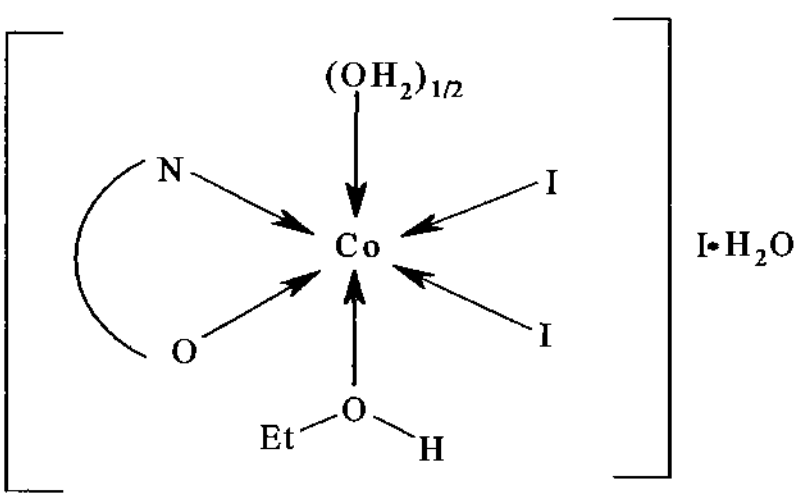


Fig. 51. Infrared spectrum of $[Co(C_7H_{10}N_3O)I_2.1/2H_2O.1/2EtOH]\ I.H_2O$ in KBr.

The low value of magnetic moment for the Co(II) complex (1.7 B.M.) suggests the existence of one unpaired electron. This may occur by assuming that the environment around the Co(II) ion acts as a strong ligand forming low-spin configuration $(t_{2g}^{6}\,e_g^{1})$[56,57].

The electronic spectrum of the Co(II) complex, $[Co(C_7H_{10}N_3O)I_2.1/2EtOH.1/2H_2O]I.H_2O$, in Nujol mull shows two bands at 15822 cm^{-1} (632 nm) and 18083 cm^{-1} (553 nm) assigned to $2A_{1g} \longrightarrow {}^2T_{1g}\,({}^2E_g)$ and ${}^2A_{1g} \longrightarrow {}^2T_{1g}$ transitions[54]. The ^{1}H-NMR spectrum of the Co(II) complex in d_6-DMSO (Fig. 52) shows singlet signals at 3.65, 5.67 and 9.08 p.p.m., downfield with respect to TMS, assignable to the protons of NH_2, CH_2 and NH groups, respectively. Also, the spectrum shows signals at 2.51, 4.50 and 5.5 p.p.m. attributed to the protons of CH_3 (ethanol), CH_2 (ethanol) and OH (ethanol), respectively. The broad signal at 7.1 p.p.m. is assigned to the OH group (H_2O). Finally, the multiple signals in the 7.81-8.91 p.p.m. region are assigned to the protons of pyridine group. All these foundations suggest structure 28 for the Co(II) complex.



(structure 28)

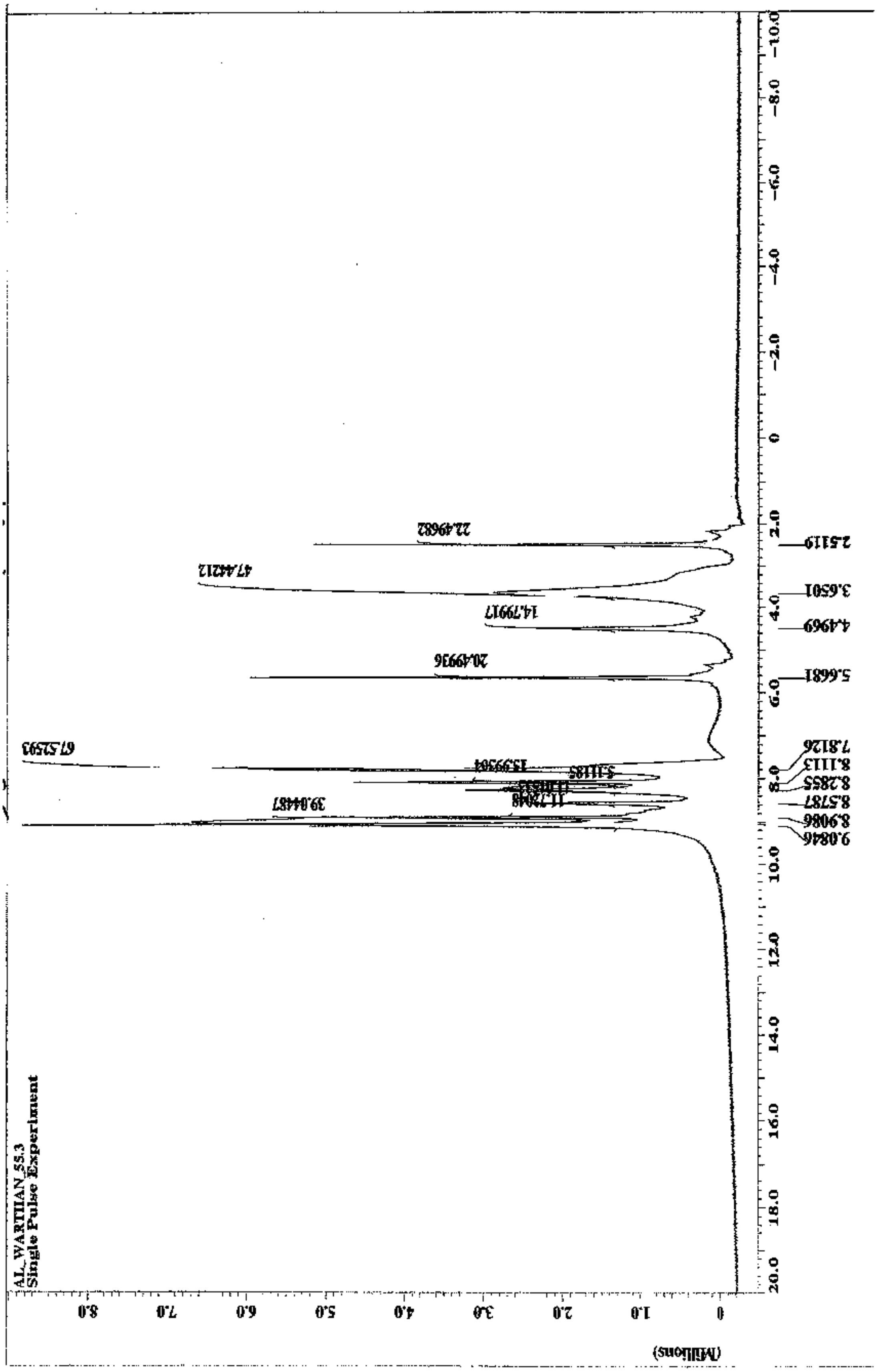


Fig. 52. [1]H-NMR spectrum of $[Co(C_7H_{10}N_3O)I_2.1/2\ H_2O.\ 1/2\ EtOH]I.\ H_2O$ in d_6-DMSO.

The IR spectrum of the Cu(II) complex, $[Cu(C_7H_{10}N_3O)I_2]$ $[Cu.I_2.1/2EtOH]2H_2O$, in KBr (Fig. 53) is similar to the previous one and shows a negative shifts of both the carbonyl oxygen and NH_2 groups to lower wavenumbers and these bands are observed at 1681 and 1625 cm^{-1}, respectively. Also, the observation of the bands at 3257 and 3210 cm^{-1} attributable to $\upsilon_{as}(NH_2)$ and $\upsilon_s(NH_2)$ vibrations to lower wavenumber in comparison to those observed in the spectrum of the free ligand at 3459 and 3343 cm^{-1}.

The electronic spectrum of the copper complex in Nujol mull (Fig. 54) shows a broad band centered at 15129 cm^{-1} (661 nm) with a several weak bands in the 500 - 600 nm region. This suggests the existence of a pseudo-tetrahedral geometry around the Cu(II) ion(55). The low value of magnetic moment (1.1 B.M.) suggests either the existence of a polymeric structure with copper - copper interaction or the existence of a mixed structure of Cu(II) and Cu(I) ions. The last proposal is more favorable than the first one. The low molar conductance value in DMF (28.4 $\Omega^{-1}.cm^2.mol^{-1}$) suggests the existence of 1:1 electrolyte(41).

The ^1H-NMR spectrum of the complex in d_6-DMSO (Fig. 55) shows three singlet signals at 11.03, 5.61 and 2.38 p.p.m, downfield with respects to TMS, with intensities 1:2:2 assignable to the protons of NH, CH_2 and NH_2 groups. Also, the spectrum shows three signals with intensities (3:2:1) at 2.50, 5.43 and 5.72 p.p.m. assignable to the protons of CH_3, CH_2 and OH for the ethanol molecule. The multiple signals in the 8.1- 9.00 p.p.m. region is assigned to the protons of the pyridyl group. The broad signal at 4.65 p.p.m. is assigned to the protons of the H_2O molecule.

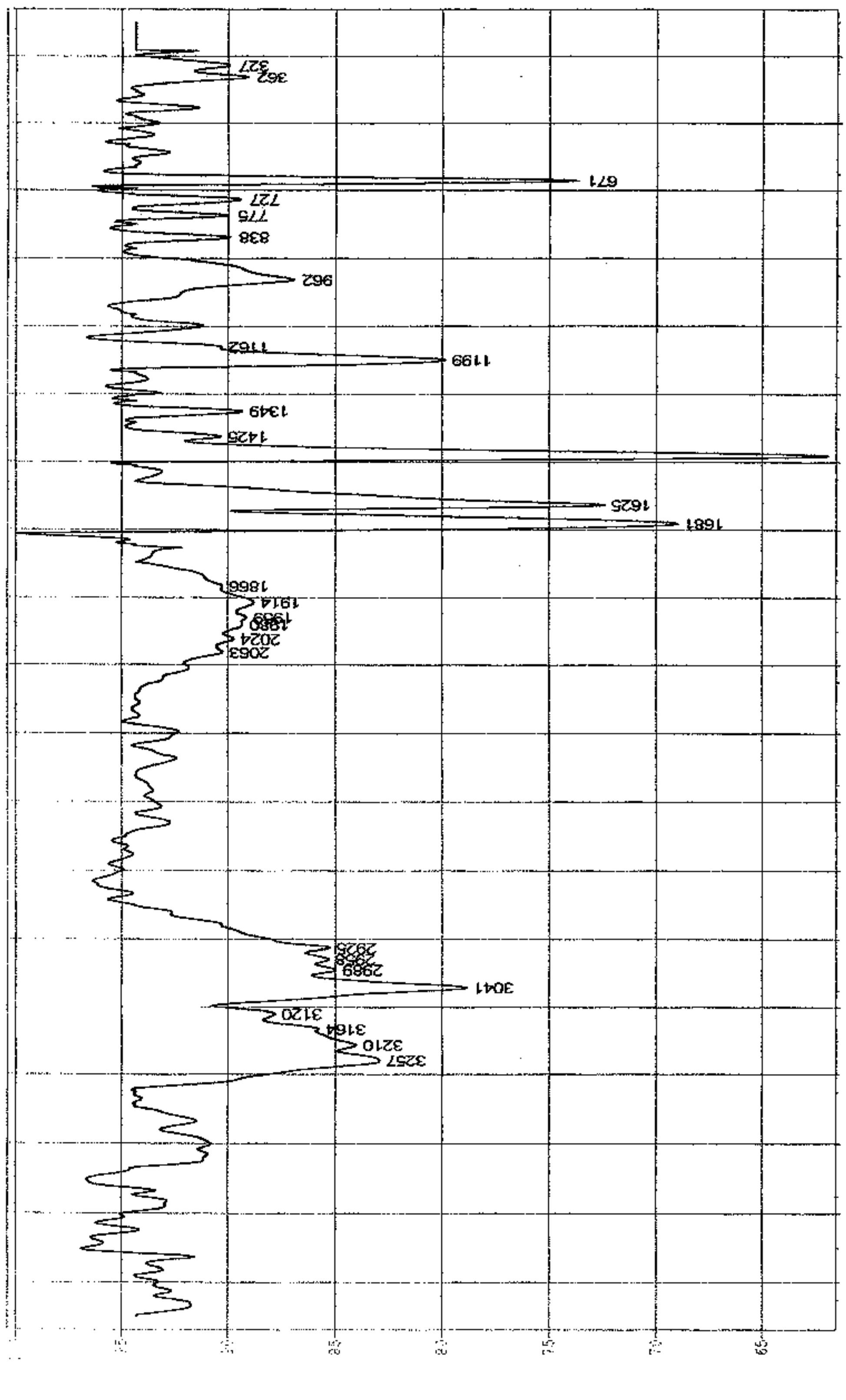


Fig. 53. Infrared spectrum of $[Cu(C_7H_{10}N_3O)I_2][CuI_2.1/2EtOH]\ 2H_2O$ in KBr.

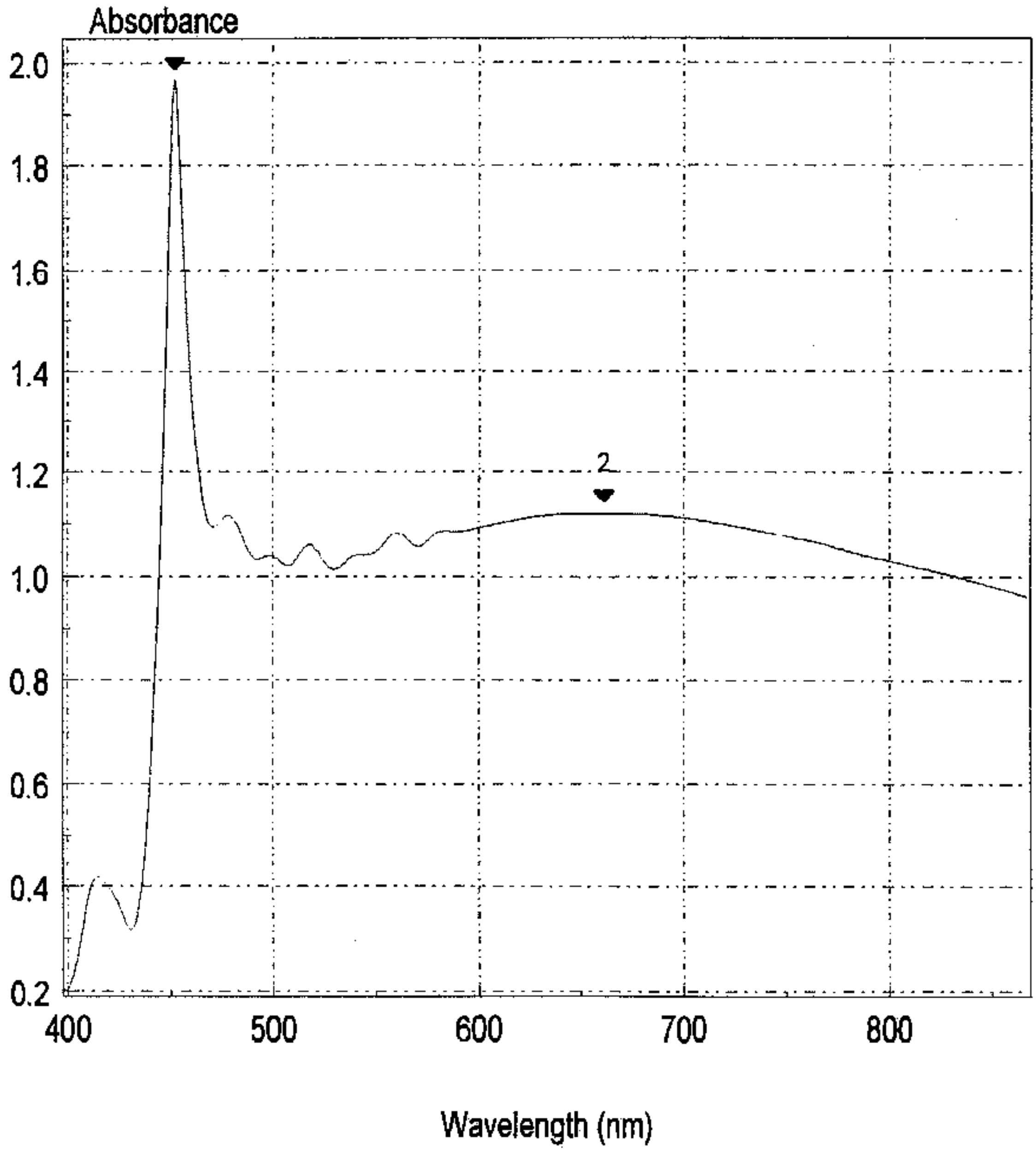


Fig. 54. Electronic spectrum of [Cu($C_7H_{10}N_3O$)I_2] [Cu I_2.1/2 EtOH]$2H_2O$ in KBr.

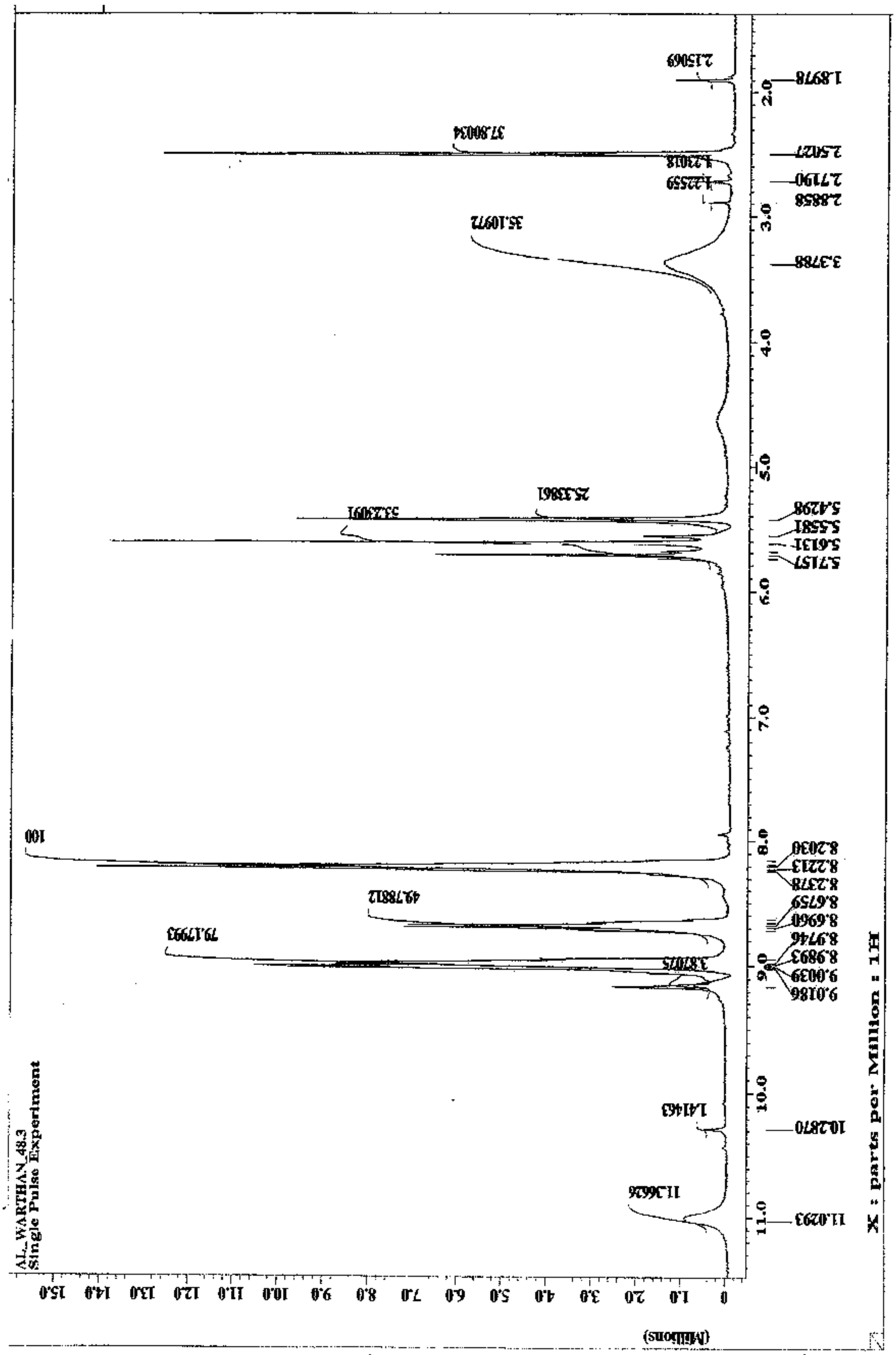


Fig. 55. ^{1}H-NMR spectrum of $[Cu(C_7H_{10}N_3O)I_2]$ $[CuI_2.$ 1/2 $EtOH]2H_2O$ in d_6-DMSO.

Finally, the latter Cu(II) complex with the general formula, $[Cu(C_7H_{10}N_3O)I_2][CuI_3.1/2EtOH]$, differ from the previous in the nature of the copper ion. In this case the complex contains only Cu(II) ion while the previous one contains both Cu(I) and Cu(II) ions as discussed earlier.

The IR spectrum of the Cu(II) complex in KBr (Fig. 56) is similar to the spectra of the previous two complexes (Figs. 51 and 53) in which the ligand coordinates in a bidentate manner *via* the NH_2 and CO groups forming a five-member ring around the metal ion.

In this case, the value of magnetic moment (1.3 B.M.) suggests the presence of copper-copper interaction[(46)]. Also, the value of molar conductance ($25.9\,\Omega^{-1}.cm^2.mol^{-1}$) suggests the electrolytic nature of this complex [(41)].

The ^{1}H-NMR spectrum of the Cu(II) complex in d_6 –DMSO (Fig. 57) shows also three singlet signals at 4.62, 5.71 and 10.99 p.p.m. assignable to the protons of NH_2, CH_2 and NH groups. Also, the signals at 2.50, 5.6 and 10.3 are assigned to the protons of CH_3, CH_2 and OH for the EtOH molecule. The multiple signals in the 8.2-9.01 region are assigned to the protons of the pyridyl group.

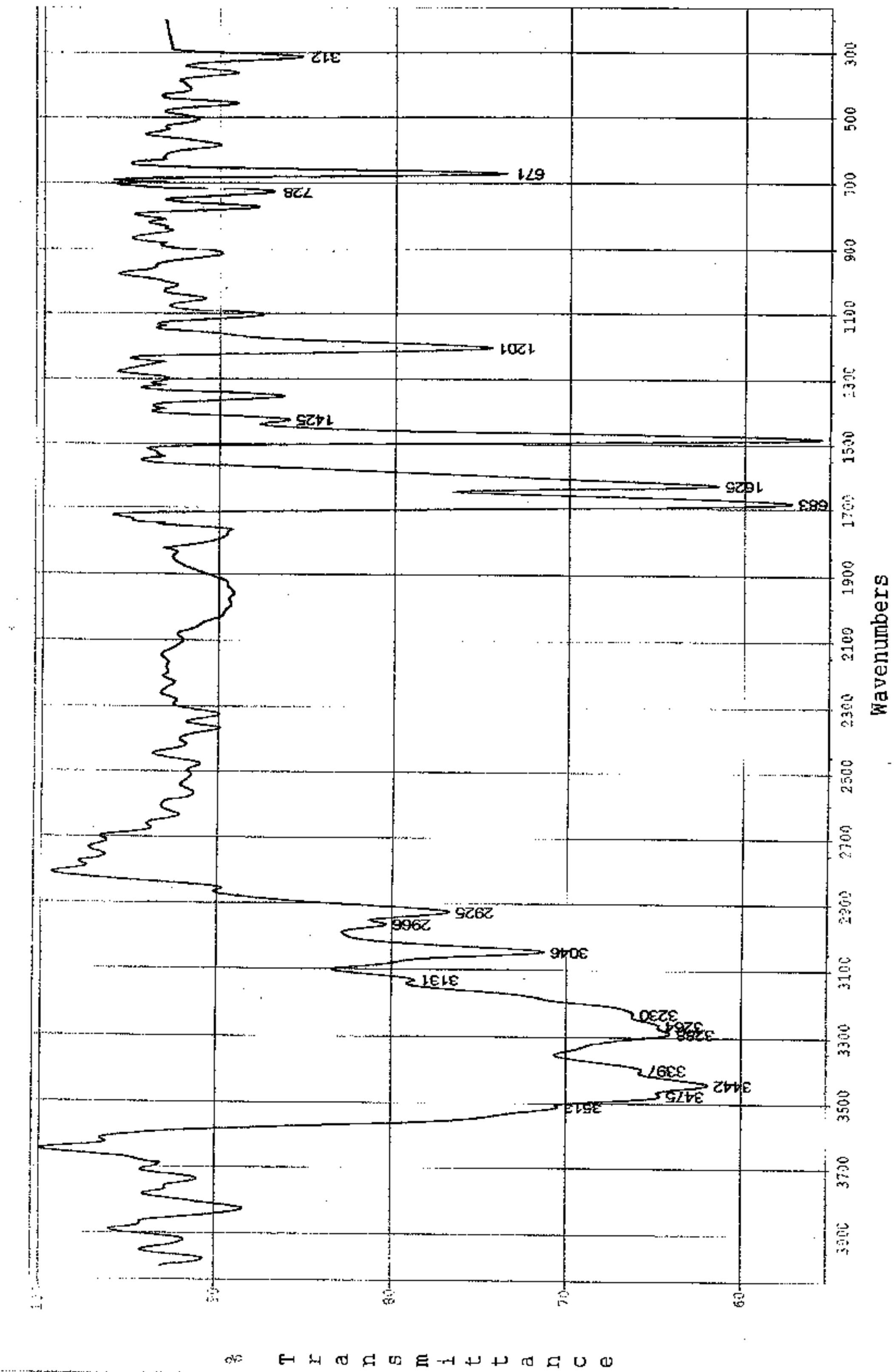


Fig. 56. Infrared spectrum of [Cu($C_7H_{10}N_3O$) I_2] [CuI_3. 1/2EtOH] in KBr.

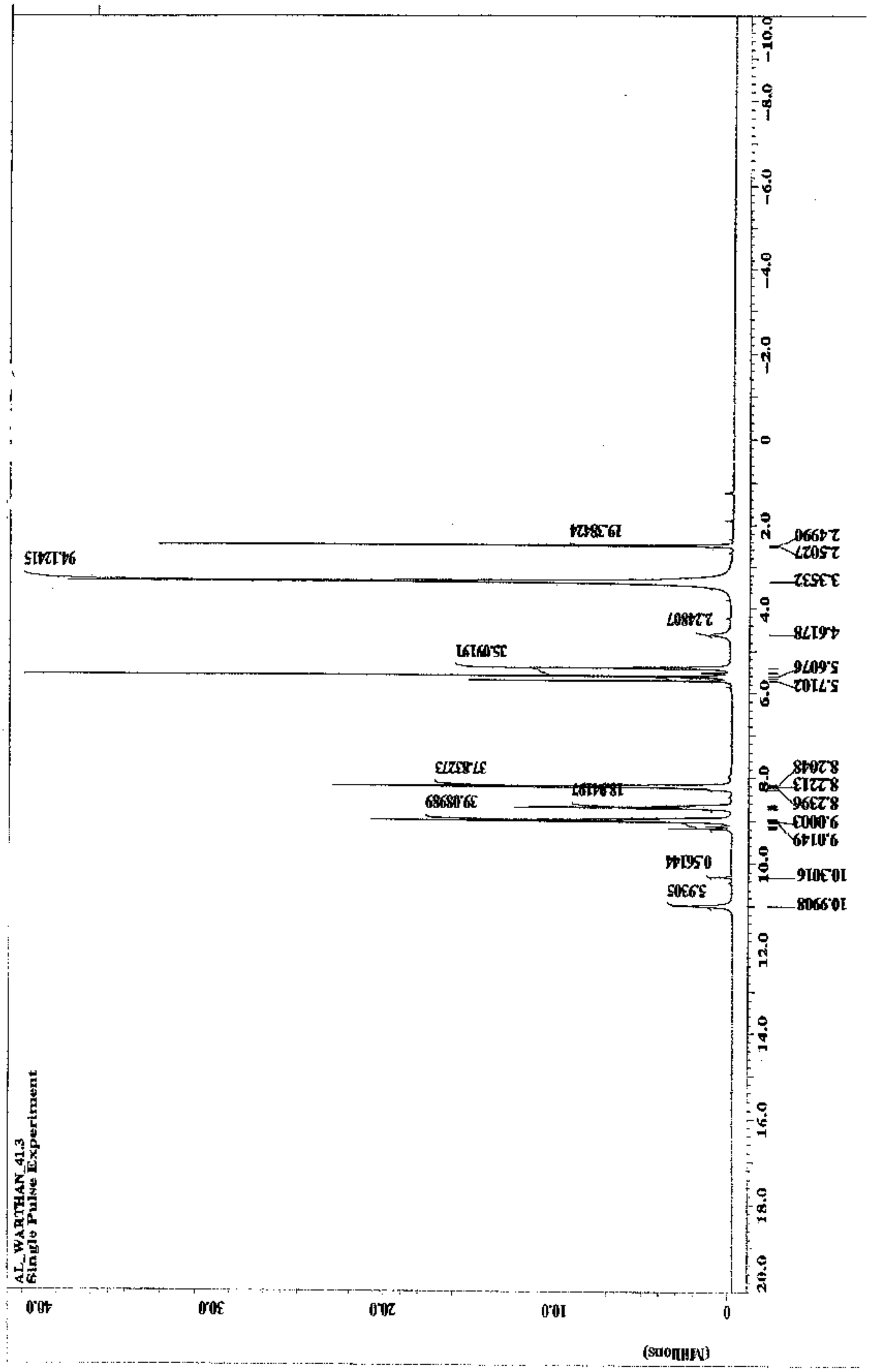


Fig. 57. ^{1}H **- NMR spectrum of [Cu ($C_7H_{10}N_3O$)I_2] [CuI_3. 1/2EtOH] in d_6 - DMSO.**

5.2. Spectral, Conductance and Magnetic Moments for the Complexes Derived from HPPTU and 3-HPPTU.

The IR spectrum of the selmon Cu(I) complex, $[Cu(C_{12}H_{11}N_3OS)I.H_2O]4H_2O$, in KBr (Fig. 58) shows that the ligand behaves in a bidentate manner *via* the NH(1) and OH groups forming five-member ring around the Cu(I) ion. The spectrum shows a negative shifts of both the NH(1) and OH groups to lower wavenumbers and are observed at 3207 and 3300 cm^{-1}, respectively. On the other hand, the bands due to the thioketo group (CS) remain more or less at the same positions and observed at 1255 and 752 cm^{-1}. The positive shift of the azomethine group of the pyridyl group is taken as evidence that the pyridyl nitrogen does not participate in bonding. This band is observed at 1652 cm^{-1} while it observed at 1646 cm^{-1} in the free ligand. The bands observed at 480, 335 and 215 are assigned to υ(Cu-O)(42), υ(Cu-N)(43) and υ(Cu-I)(47) vibrations, respectively. The value of molar conductance (10.2 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a non–electrolytic nature(41). The diamagnetic nature of this complex suggests that the Cu(II) complex is reduced to Cu(I).

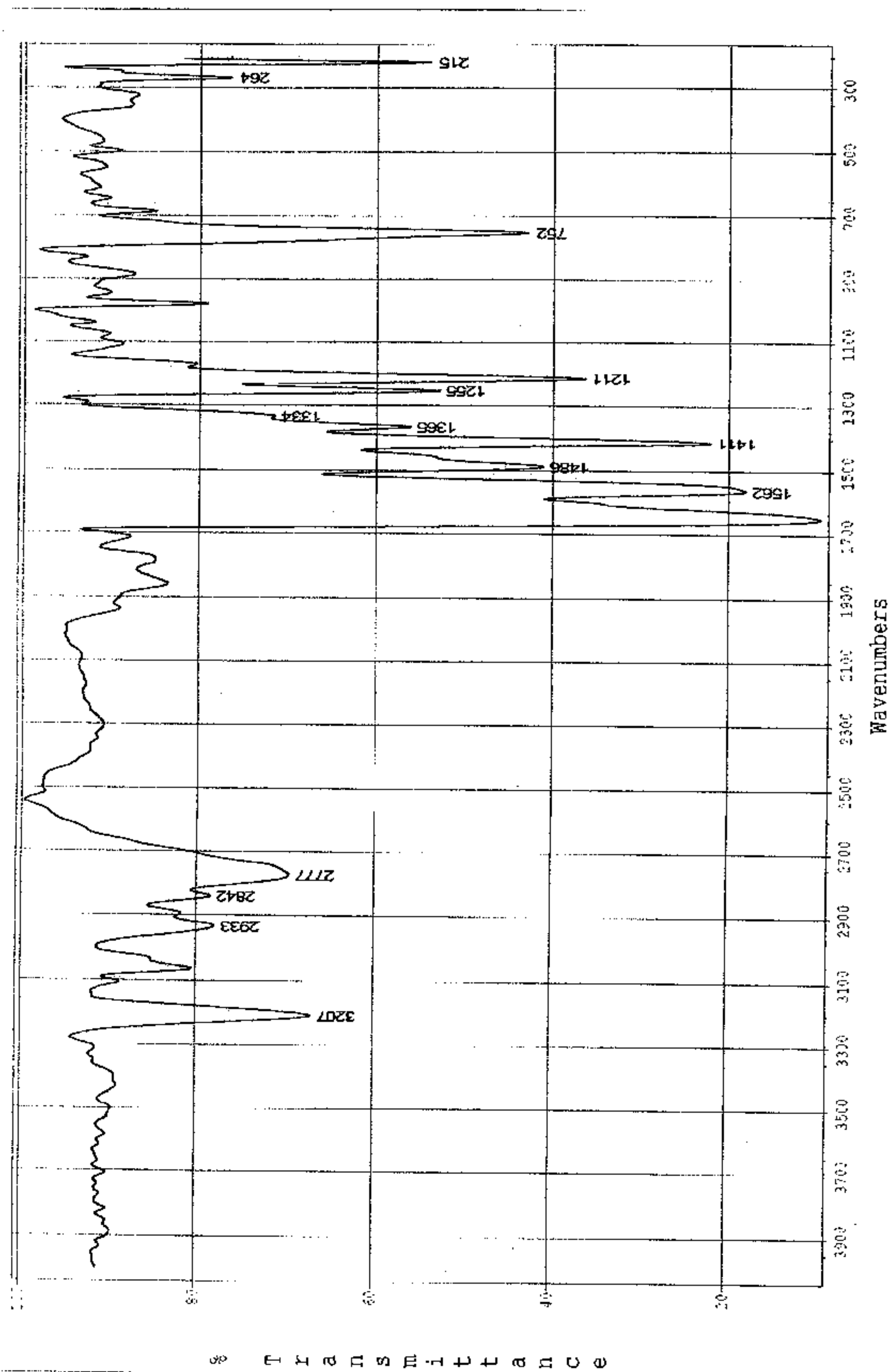
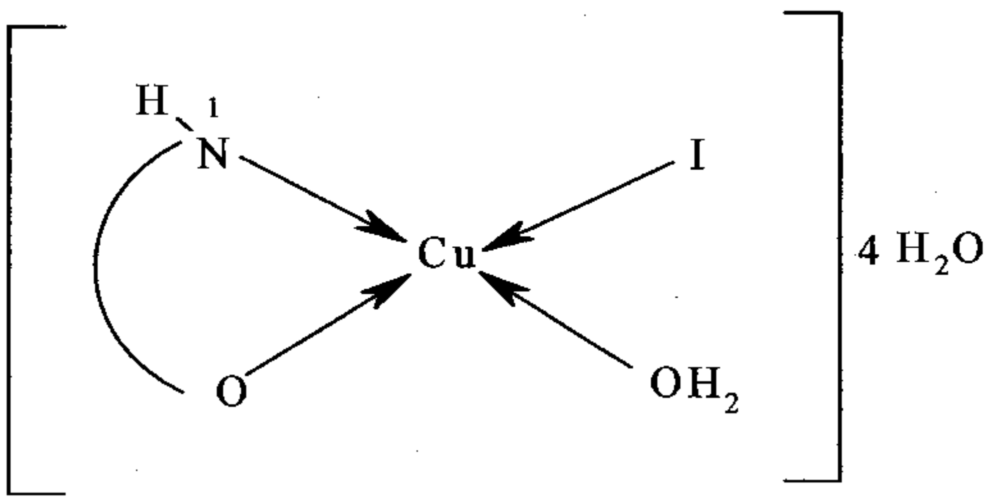


Fig. 58. Infrared spectrum of [Cu($C_{12}H_{11}N_3OS$) I. H_2O] $4H_2O$ in KBr.

The ^{1}H-NMR spectrum of the Cu(I) complex in d_6–DMSO (Fig. 59) shows two singlet signals at 10.97 and 8.27 p.p.m., downfield with respect TMS, assigned to the protons of NH(1) and OH groups, respectively. Also, the doublet signal at 7.87 p.p.m. is assigned to the proton of NH(2) group. All these foundations suggest a square-planar geometry around the Cu(I) ion as shown in structure 29.



(structure 29)

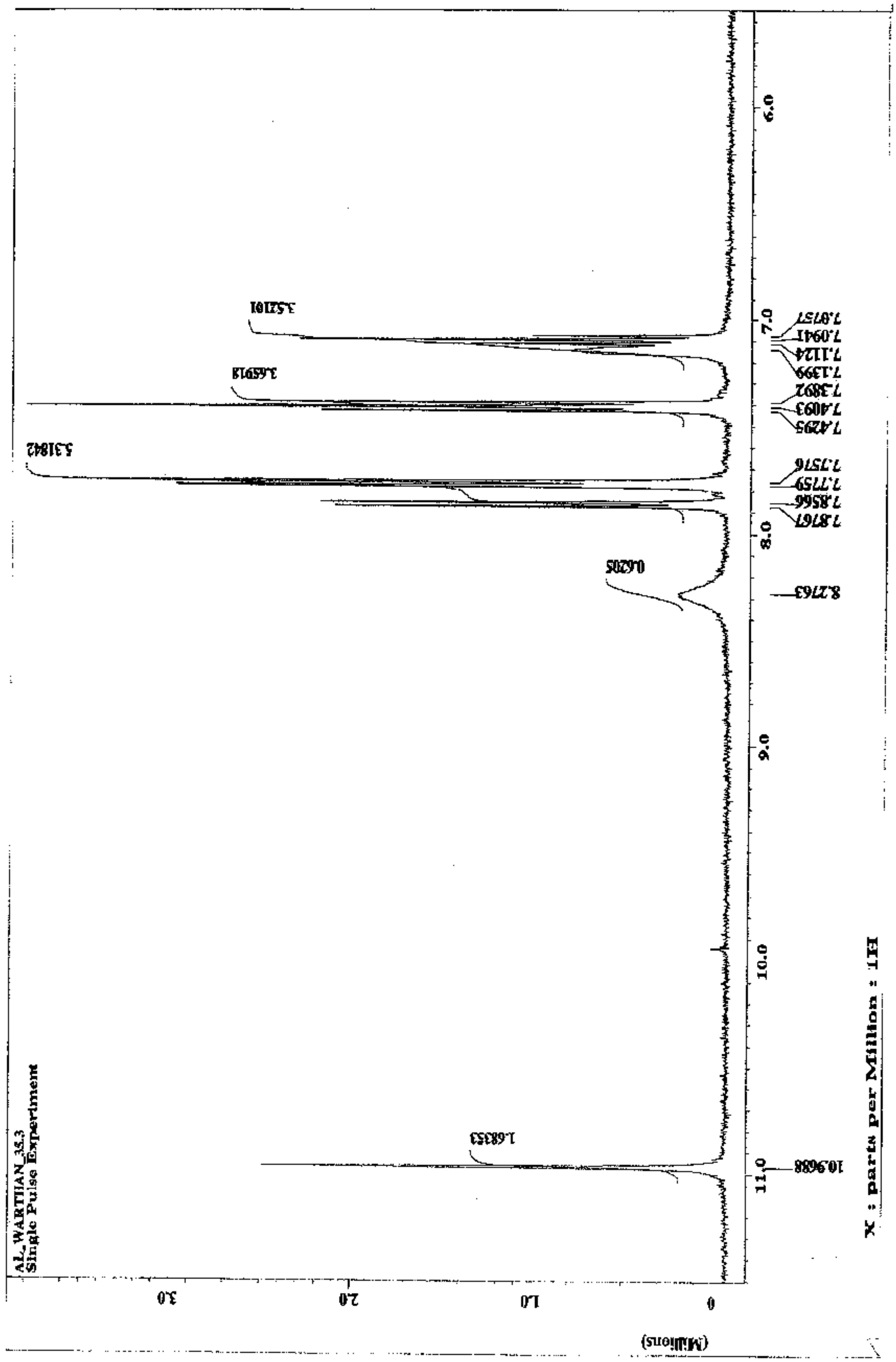


Fig. 59. ^{1}**H – NMR spectrum of [Cu($C_{12}H_{11}N_3OS$) I.H_2O] 4H_2O in d_6 – DMSO.**

The IR spectrum of the green Co(III) complex, $[Co(C_{12}H_{11}N_3OS)_4I_2]I$, in KBr (Fig. 60) shows that the ligand (HPPTU) coordinates in a monodentate manner *via* the NH(1) group. The spectrum shows that the positions of the NH(2), OH and CS groups remain unchanged indicating that these groups does not participate in bonding. Also, the spectrum shows a weak band at 380 cm^{-1} assigned to the υ(Co-N)(42). The diamagnetic nature of the cobalt complex suggests the oxidation of Co^{2+} to Co^{3+}. Also, it suggests that HPPTU acts as a strong ligand towards the Co(III) forming the $t_{2g}^6\ e_g^o$ configuration(58-59). The molar conductance value in DMF (34.3 $\Omega^{-1}.cm^2.mol^{-1}$) suggests 1:1 electrolyte (41).

The ^1H–NMR spectrum of the Co(III) complex in d_6–DMSO (Fig. 61) shows three signals at 11.00, 8.23 and 7.79 p.p.m., downfield with respect to TMS, assignable to the protons of OH, NH(1) and NH(2), respectively. The multiple signals in the 7.08-7.79 p.p.m. are assigned to the protons of the pyridyl and phenyl groups. All these foundations suggest structure 30 for this complex.

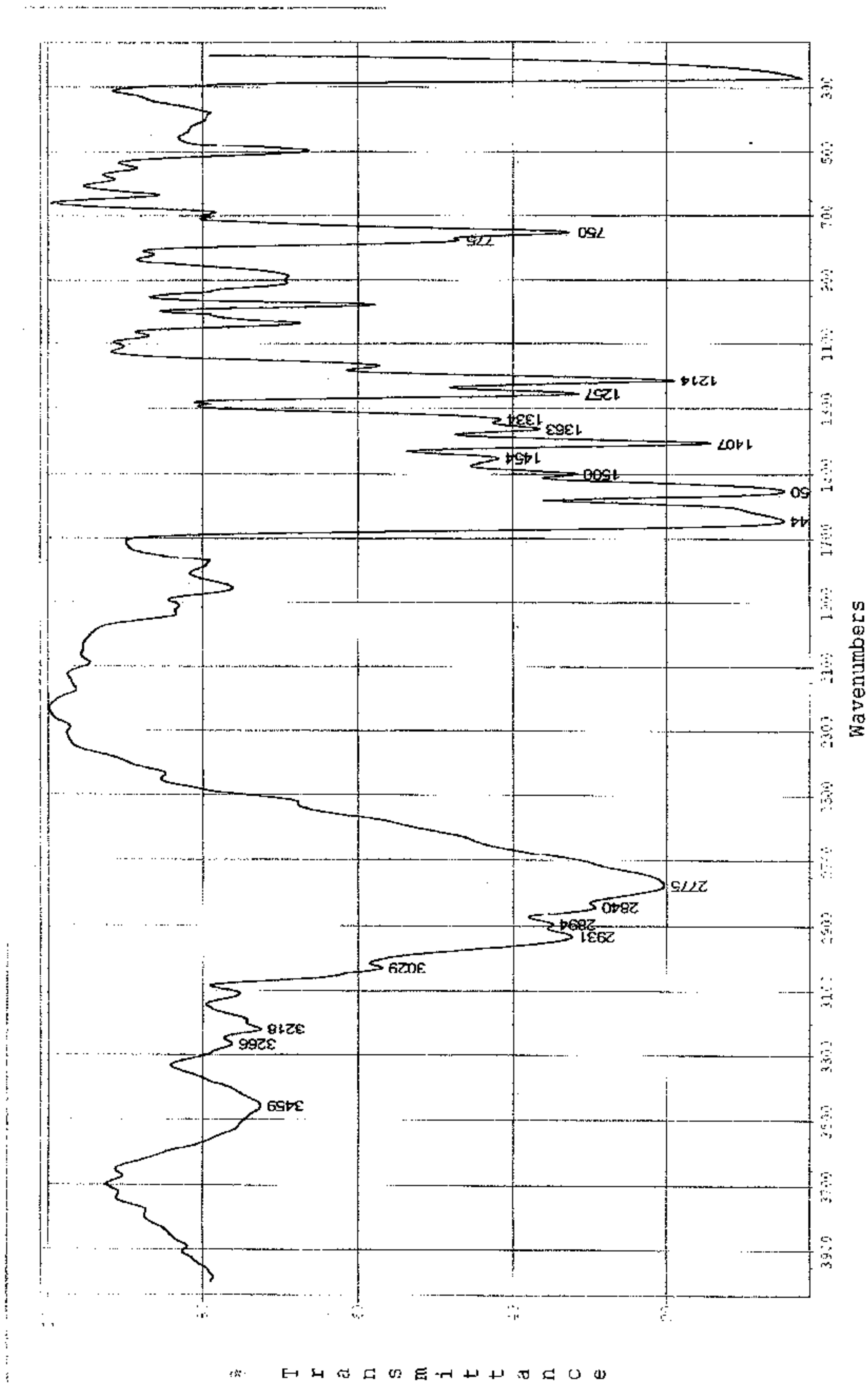


Fig. 60. Infrared spectrum of $[Co(C_{12}H_{11}N_3OS)_4I_2]I$ in d_6 -DMSO.

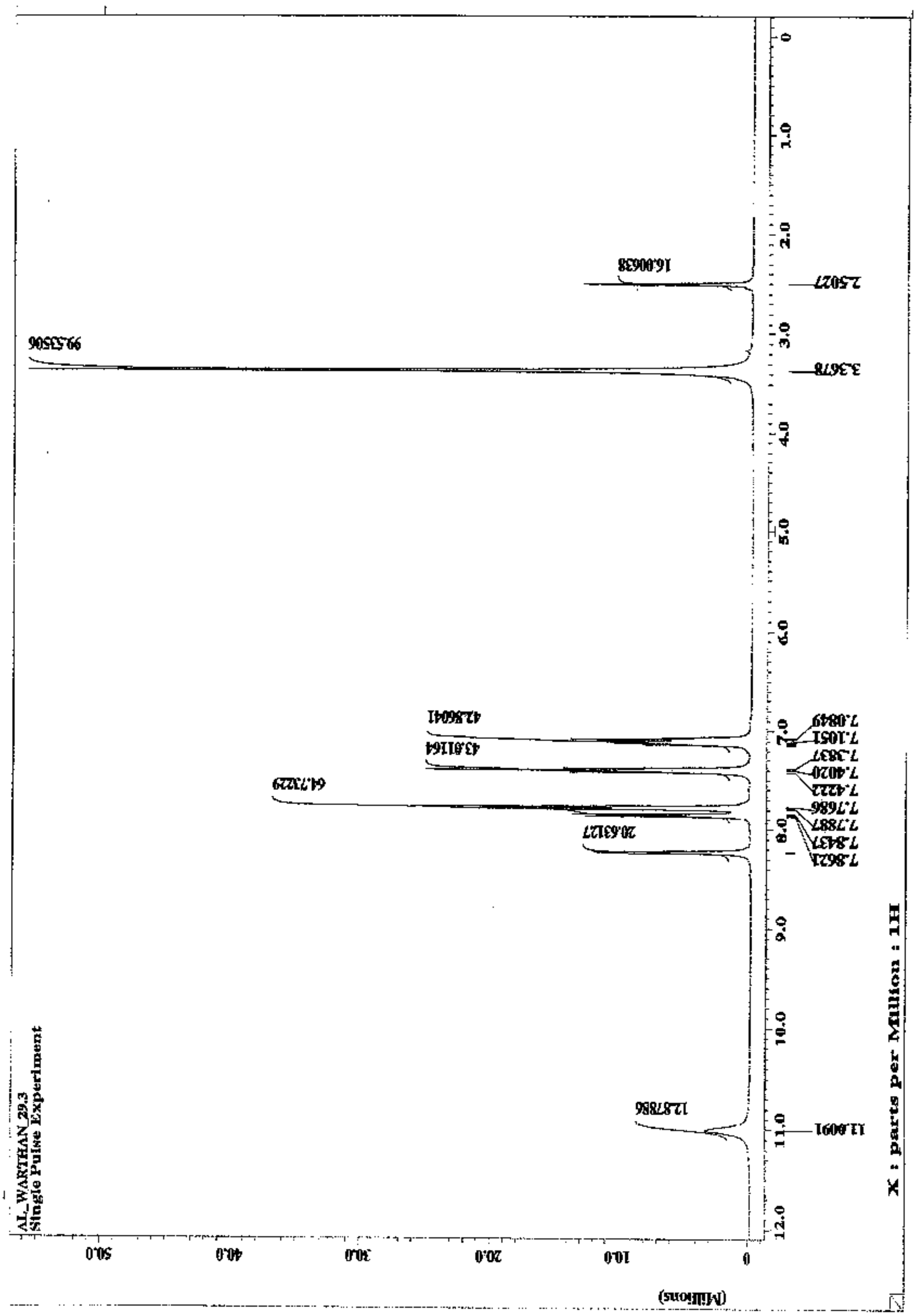
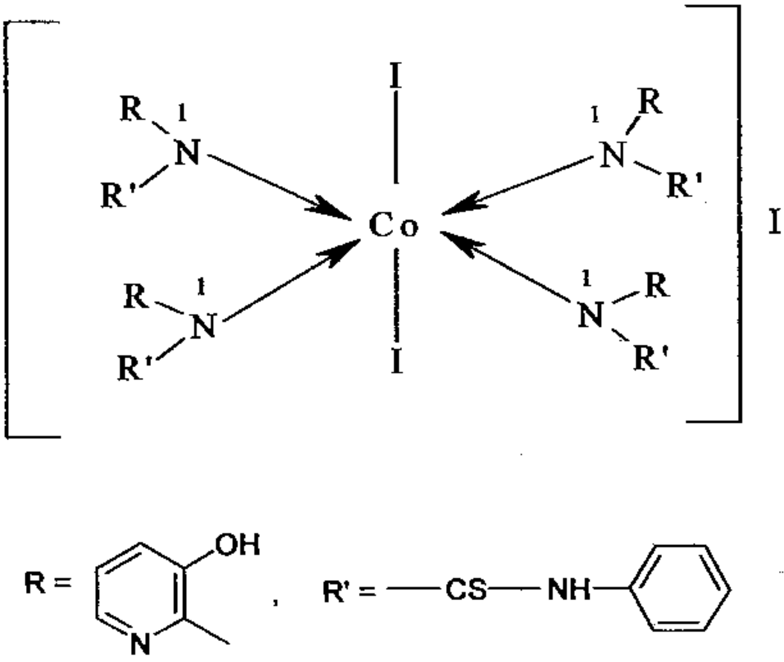


Fig. 61. ^{1}H-NMR spectrum of $[Co(C_{12}H_{11}N_3OS)_4 I_2]I$ in d_6-DMSO.



(structure 30)

The IR spectrum of the diamagnetic Cu(I) complex, $[Cu(C_{13}H_{12}N_2OS)I.H_2O]1/2H_2O$, in KBr (Fig. 62) shows that the ligand (3-HPPTU) behaves in a bidentate manner *via* the OH and NH(1) groups forming five–member ring around the Cu(I) ion. The spectrum shows a negative shifts of these bands to lower wavenumbers and are observed at 3444 and 3033 cm^{-1}. The band observed at 3492 cm^{-1} is assigned to υ(OH) vibration of the coordinated water. Also, the spectrum shows that the positions of the thioketo group remain unchanged on comparing with the spectrum of the free ligand (Fig. 6). This indicates that this group (CS) does not take part in coordination. The bands observed at 510, 443, 360 and 217 cm^{-1} are assigned to the υ(Cu-O)(H_2O), υ(Cu-O)(OH), υ(Cu-N) and υ(Cu-I) vibrations, respectively.

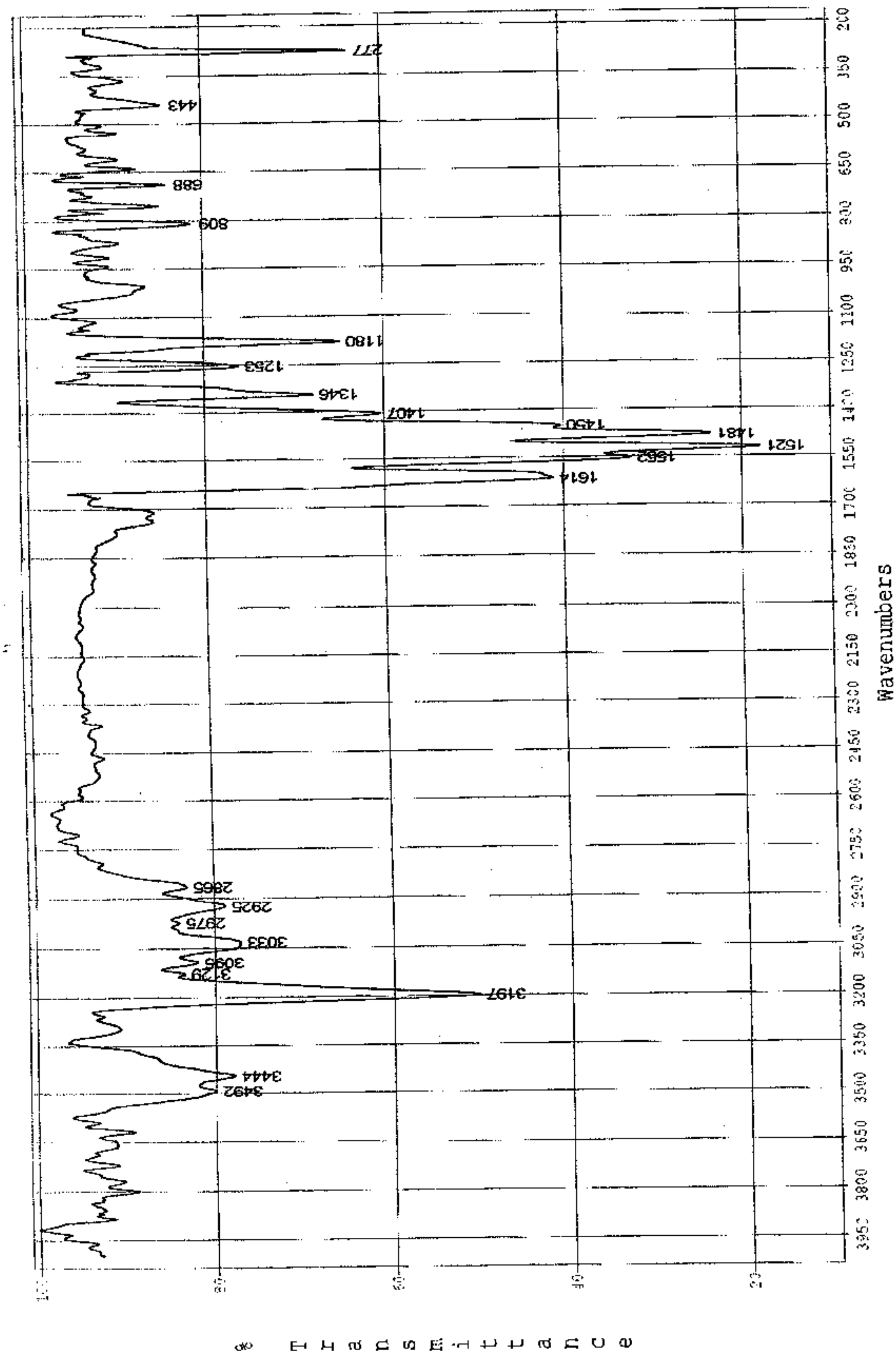
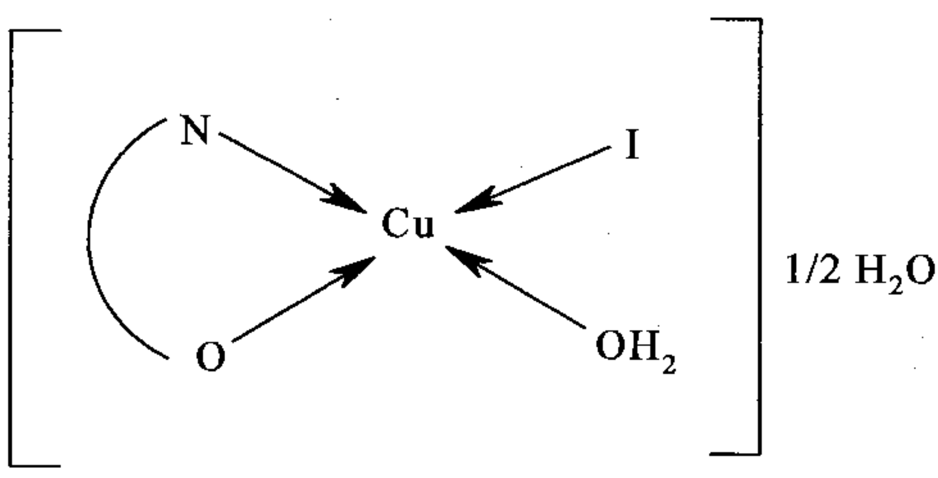


Fig. 62. Infrared spectrum of [Cu ($C_{13}H_{12}N_2OS$) I.H_2O] 1/2H_2O in KBr.

The ^{1}H-NMR spectrum of the Cu(I) complex in d_6-DMSO (Fig. 63) show three singlet signals with equal intensity at 1.78, 11.60 and 10.87 p.p.m., downfield with respect to TMS, assignable to the protons of OH, NH(1) and NH(2), respectively. The multiple signals in the 6.95 - 8.22 p.p.m. region are assigned to eight protons of the two phenyl groups. The signal at 2.51 p.p.m. is assigned to the proton of H_2O.

All these foundations suggest a square-planar geometry around the Cu(I) as shown in structure 31.

The value of molar conductance in DMF (10.9 $\Omega^{-1}.cm^2.mol^{-1}$.) suggests non-electrolytic nature of this complex[41].



(structure 31)

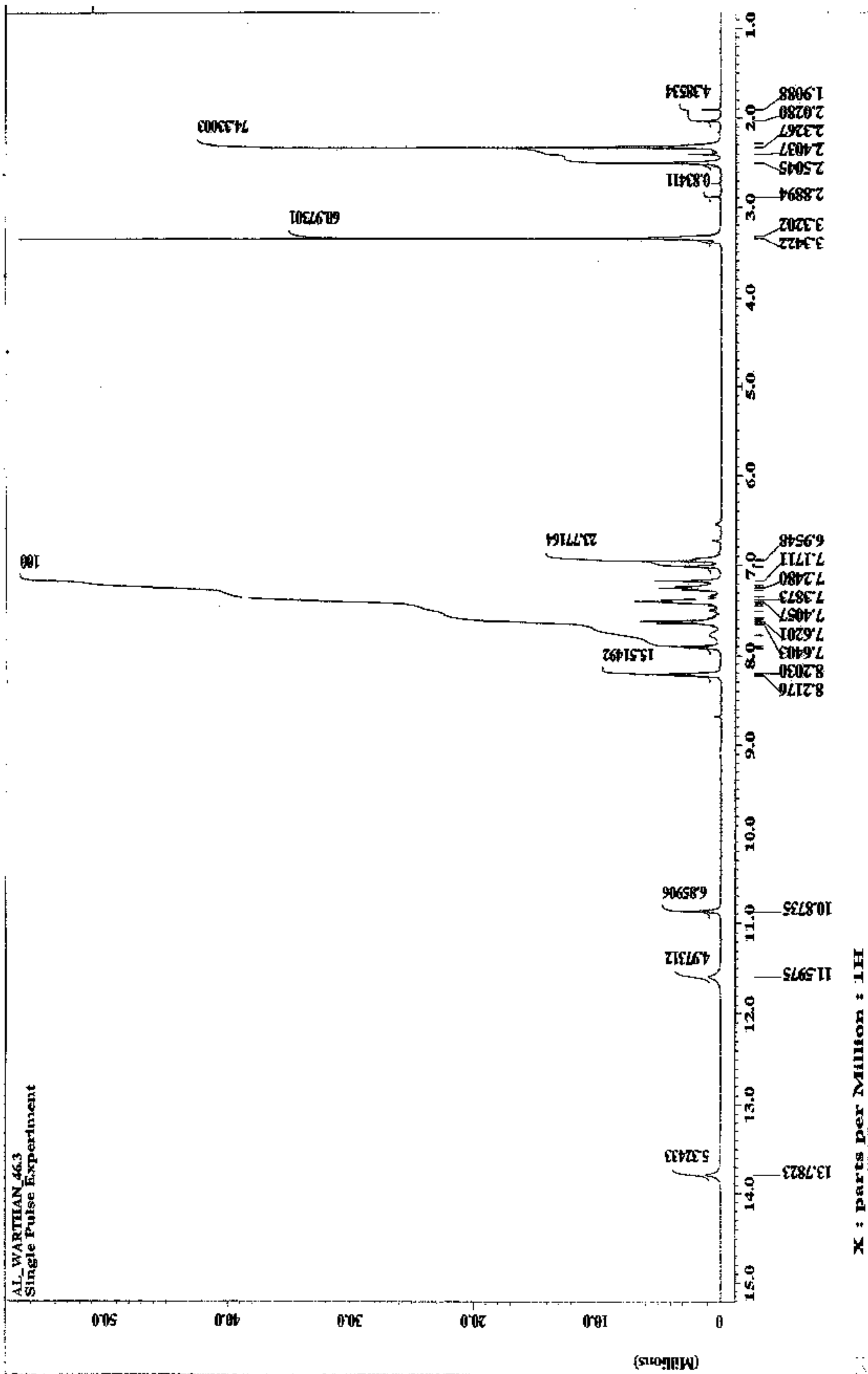


Fig. 63. ^{1}H-NMR spectrum of $[Cu(C_{13}H_{12}N_2OS)\ I.H_2O]\ ½\ H_2O$ in d_6-DMSO.

5.3. Spectral, Conductance and Magnetic Moments for the Complexes Derived from 3-MPTU and 6-MPTU.

The IR spectrum of the complex derived from 3-MPTU in KBr (Fig. 64) shows bands at 3515, 3448 and 3232 cm^{-1} assigned to the υ(OH)(H_2O), υNH(1) and υNH(2) vibrations respectively. The bands due to CS are shifted to lower wavenumbers and observed at 1238 and 725 cm^{-1} indicating the participation of the thioketo group in bonding. Also, the bands due to (C=N) are shifted to lower wavenumbers and observed at 1604 and 1523 cm^{-1} respectively. This indicates the participation of pyridyl nitrogen in bonding. All these foundations suggest that the bluish-green Cu(II) complex, $[Cu(C_{13}H_{13}N_3S)_3]I_2.1/2H_2O$, has a distorted-octahedral geometry around the Cu(II) ion and the ligand behaves in a bidentate manner *via* the CS and the pyridyl nitrogen forming a six - member ring around the Cu(II) ion.

The value of magnetic moments (1.56 B.M.) suggests the existence of a small copper-copper interaction[46]. Also, the value of molar conductance in DMF (63.3 $\Omega^{-1}.cm^2.mol^{-1}$) suggests the existence of 1:2 electrolyte [41].

The IR spectrum of the diamagnetic Cu(I) complex, $[Cu(C_{13}H_{13}N_3S)(H_2O)I]4H_2O$, in KBr (Fig. 65) shows that the ligand (6-MPTU) behaves in a bidentate manner *via* the pyridyl nitrogen and thioketo groups forming five-member ring around the Cu(I) ion. The negative shifts of those groups to lower wavenumbers confirm the participation of those two groups in bonding. The bands observed at 450, 290 and 269 cm^{-1} are assigned to υ(Cu-O)[42], υ(Cu-N)[43] and υ(Cu-S)[57] vibrations, respectively.

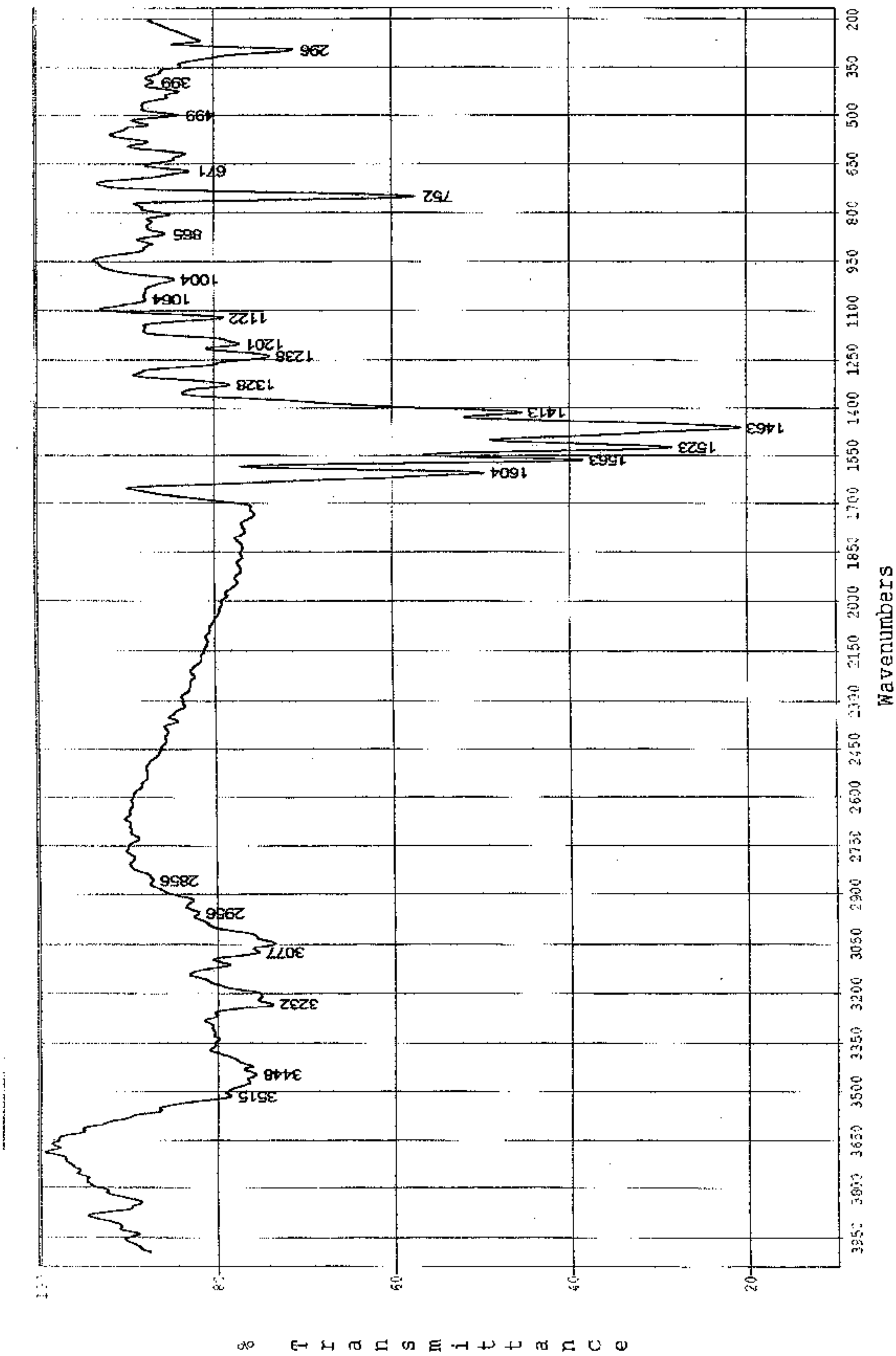


Fig. 64. Infrared spectrum of $[Cu(C_{13}H_{13}N_3S)_3]\ I_2.\ ½\ H_2O$ in KBr.

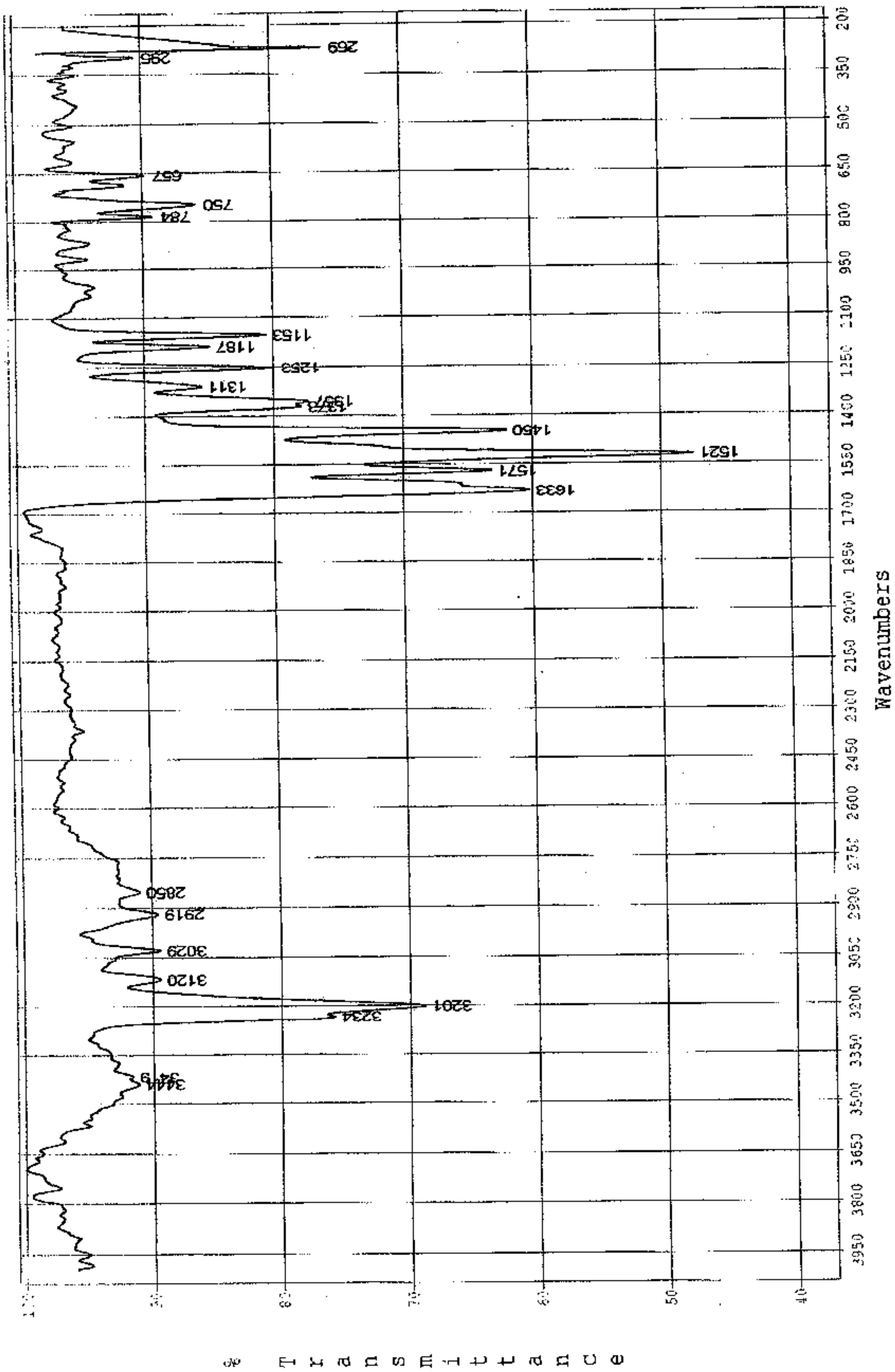
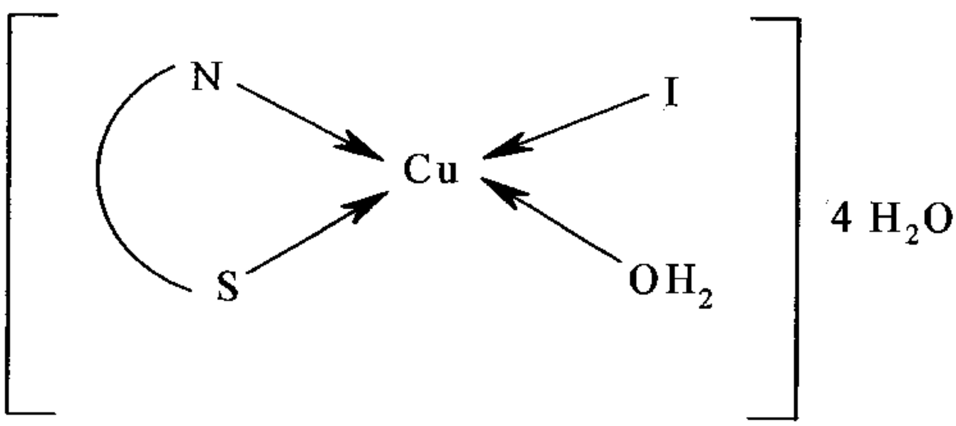


Fig. 65. Infrared spectrum of [Cu($C_{13}H_{13}N_3S$). H_2O. I] $4H_2O$ in KBr.

The ^{1}H-NMR spectrum of the pale-brown Cu(I) complex, $[Cu(C_{13}H_{13}N_3S)(H_2O)I]4H_2O$, in d_6-DMSO (Fig. 66) shows three singlet signals at 14.11, 10.82 and 2.29 p.p.m., downfield with respect to TMS, attributable to NH(1) and NH(2) and CH_3 groups, respectively. The signal at 3.68 p.p.m. is assigned to the proton of H_2O. The multiple signals in the 7.39 - 7.79 p.p.m. region are assigned to the protons of pyridyl and phenyl groups.

All these foundations as well as the value of molar conductance in DMF (8.2 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a square–planer geometry around the Cu(I) as shown in structure 32.



(structure 32)

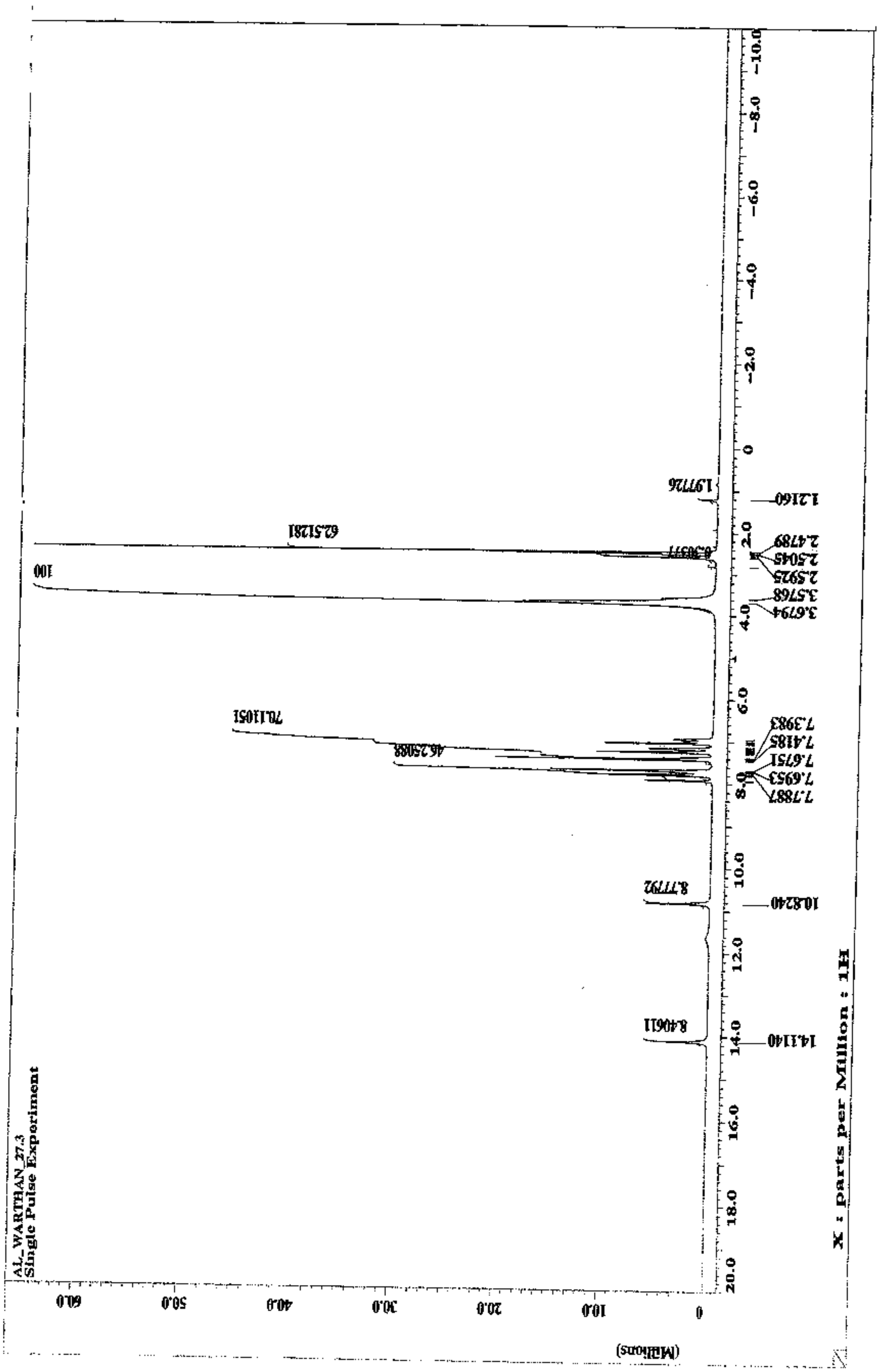


Fig. 66. ^{1}H-NMR spectrum of $[Cu(C_{13}H_{13}N_3S).\ H_2O.\ I]\ 4H_2O$ in d_6- DMSO.

The IR spectrum of the diamagnetic green Co(III) complex, $[Co(C_{13}H_{13}N_3S)(H_2O)_4]I_3.6H_2O$, in KBr (Fig. 67) shows that the ligand (6-MPTU) behaves in a bidentate manner *via* the thioketo and pyridyl nitrogen groups forming a six-member ring around the Co(III). The spectrum shows a negative shifts of the pyridyl nitrogen and CS bands to lower wavenumbers and are observed at 1623 and 1251 cm^{-1} respectively. Doubtless the participation of the thioketo group in bonding affects the two neighbour NH [NH(1) and NH(2)] groups which are observed at 3199 and 3041 cm^{-1} are assigned to υ(Co-O) (H_2O), υ(Co-N) and υ(Co-S)[(60)] vibrations, respectively.

The molar conductance value for the Co(III) complex (107.9 $\Omega^{-1}.cm^2.mol^{-1}$) suggests 1:3 electrolyte[(41)]. The ^{1}H-NMR spectrum in d6-DMSO (Fig. 68) shows three singlet signals at 14.21, 10.85 and 2.47 p.p.m., downfield with respect of TMS, assigned to the protons of NH(2), NH(1) and CH_3 groups. The multiple signals in the 6.95-7.79 p.p.m. region are assigned to the protons of the pyridyl and phenyl groups.

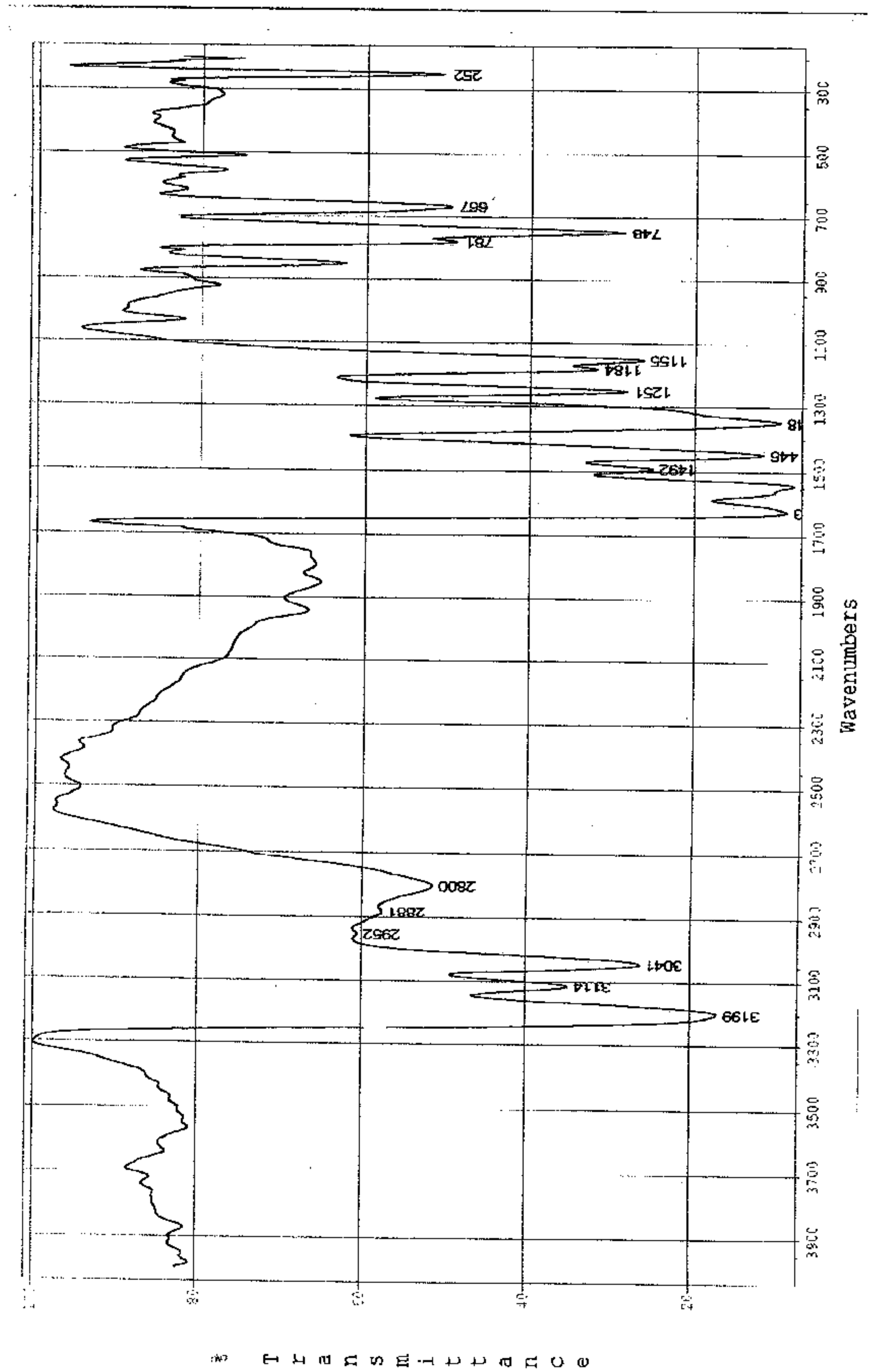


Fig. 67. Infrared spectrum of $[Co_2(C_{13}H_{13}N_2S)(H_2O)_4]\ I_3 .\ 6H_2O$ in KBr.

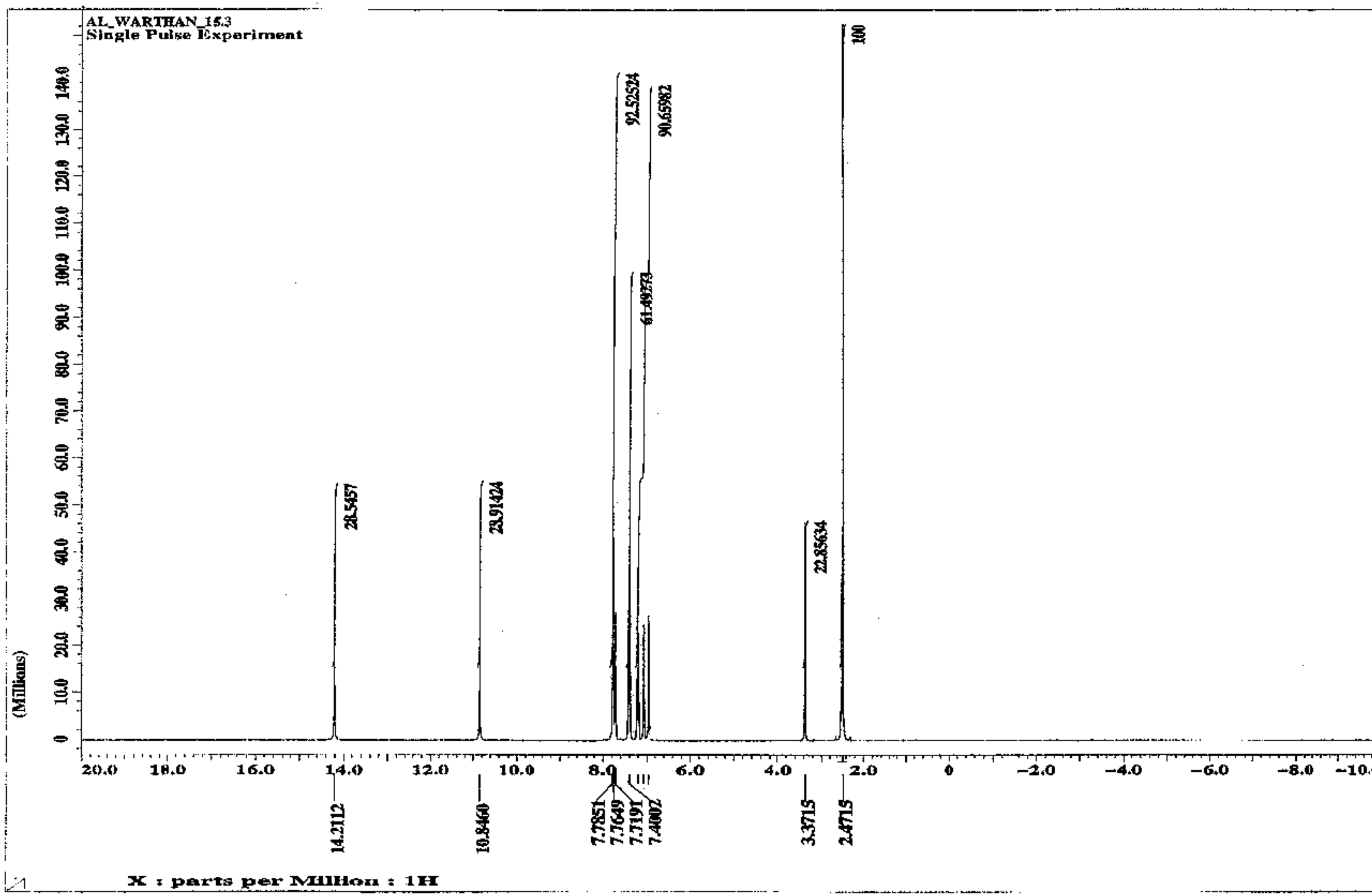
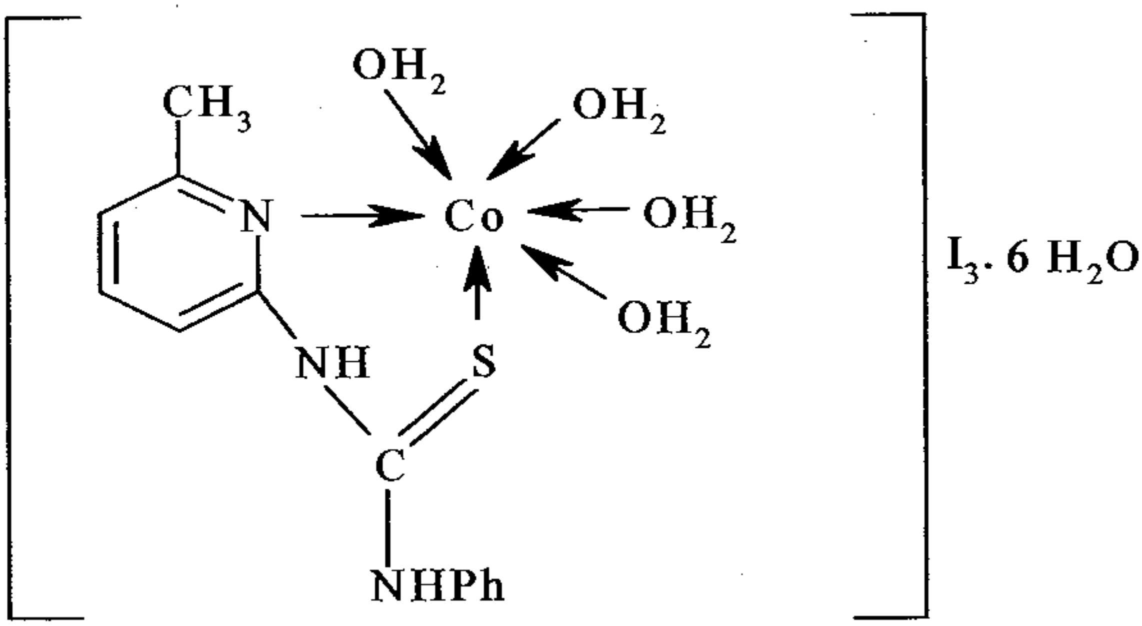


Fig. 68. ^{1}H-NMR spectrum of $[Co_2(C_{13}H_{13}N_2S)(H_2O)_4]I_3 . 6H_2O$ in d_6-DMSO.

All these foundations suggests structure 33 for the Co(III) complex. .



(structure 33)

5.4. Spectral, Conductance and Magnetic Moments for the Complexes Derived from ATHTC.

The IR spectrum of the Co(III) complex, $[Co(C_9H_{19}N_4OS)I_3.1/2EtOH]I$, in KBr (Fig. 69) shows that the ligand (ATHTC) coordinates in a bidentate manner *via* the thioketo and NH(1) forming a five–member ring around the Co(III) ion. The spectrum shows that the positive shift of the carbonyl oxygen to higher wavenmber (1711 cm^{-1}) indicating that this group does not take part in coordination. On the other hand, the bands due to N-C=S and CS groups are shifted to lower wavenumbers and are observed at 1523 and 1189 cm^{-1}. The bands observed at 460, 340, 283 and 252 cm^{-1} are assigned to υ(Co-O)[42], υ(Co-S)[57], υ(Co-N)[43] and υ(Co-I)[47] vibrations, respectively. The band at 3210 cm^{-1} in the free ligand due to NH(1) is shifted to lower wavenumber (3160 cm^{-1}) suggesting the involvement of this group in bonding.

The ^{1}H-NMR spectrum of the Co(III) complex in d_6–DMSO (Fig. 70) shows three singlet signals at 10.56, 9.65 and 8.51 p.p.m., downfield with respect to TMS. The former two signals [NH(1), NH(2)] are shifted upfield on complexation indicating the participation of NH(1) in bonding and consequently the NH(2) is affected. The signal due to NH(4) remains unchanged on complexation. The spectrum shows also signals at 5.74 (quartet), 5.04 (triplet), 4.23 (doublet), 4.68 (singlet) and 3.26 (singlet), downfield with respect to TMS, assignable to the protons of CH= , $NHCH_2$, $=CH_2$, $N.CH_2$ and CH_3, respectively.

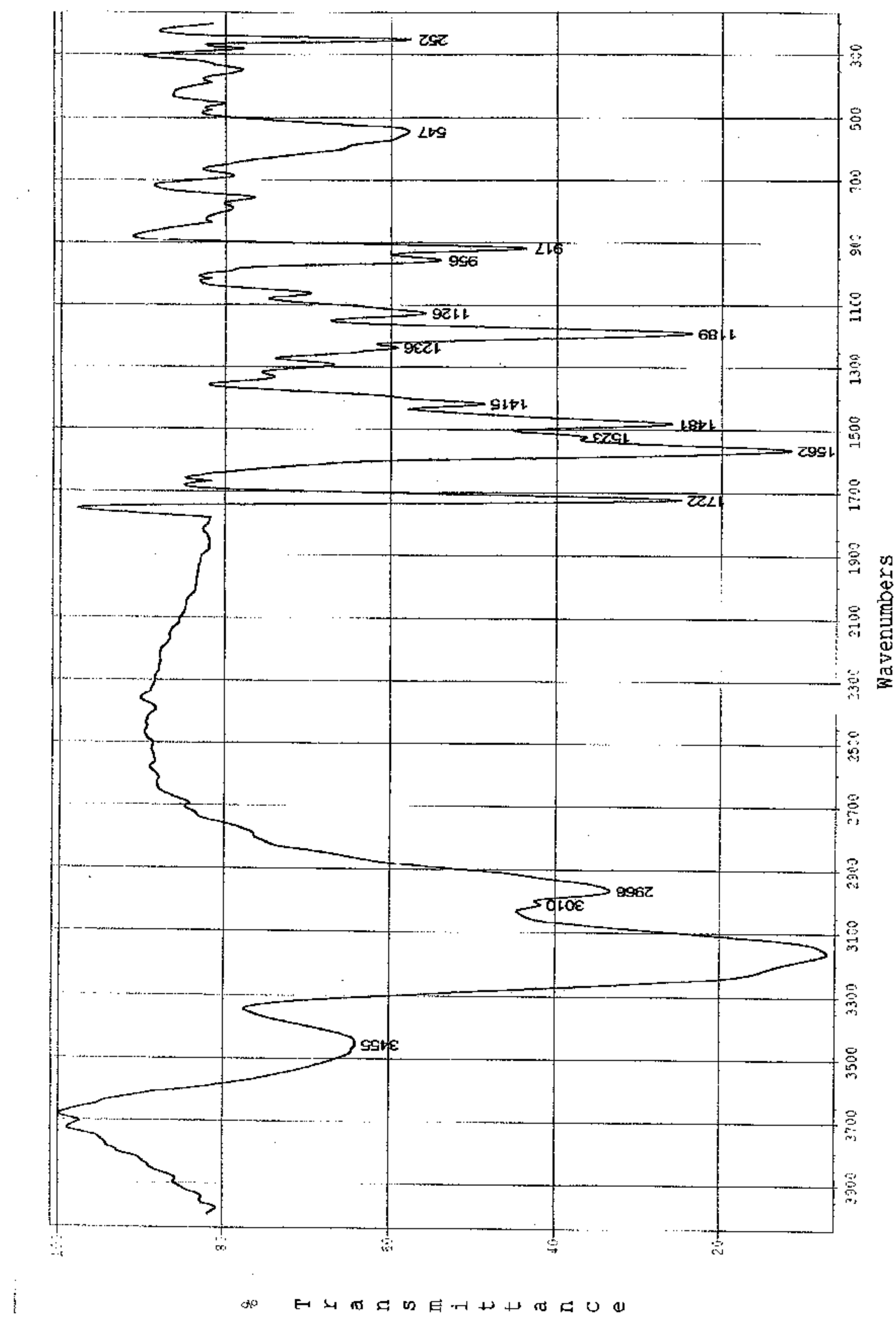


Fig. 69. Infrared spectrum of [Co($C_9H_{19}N_4OS$) I_3. ½ EtOH] I in KBr.

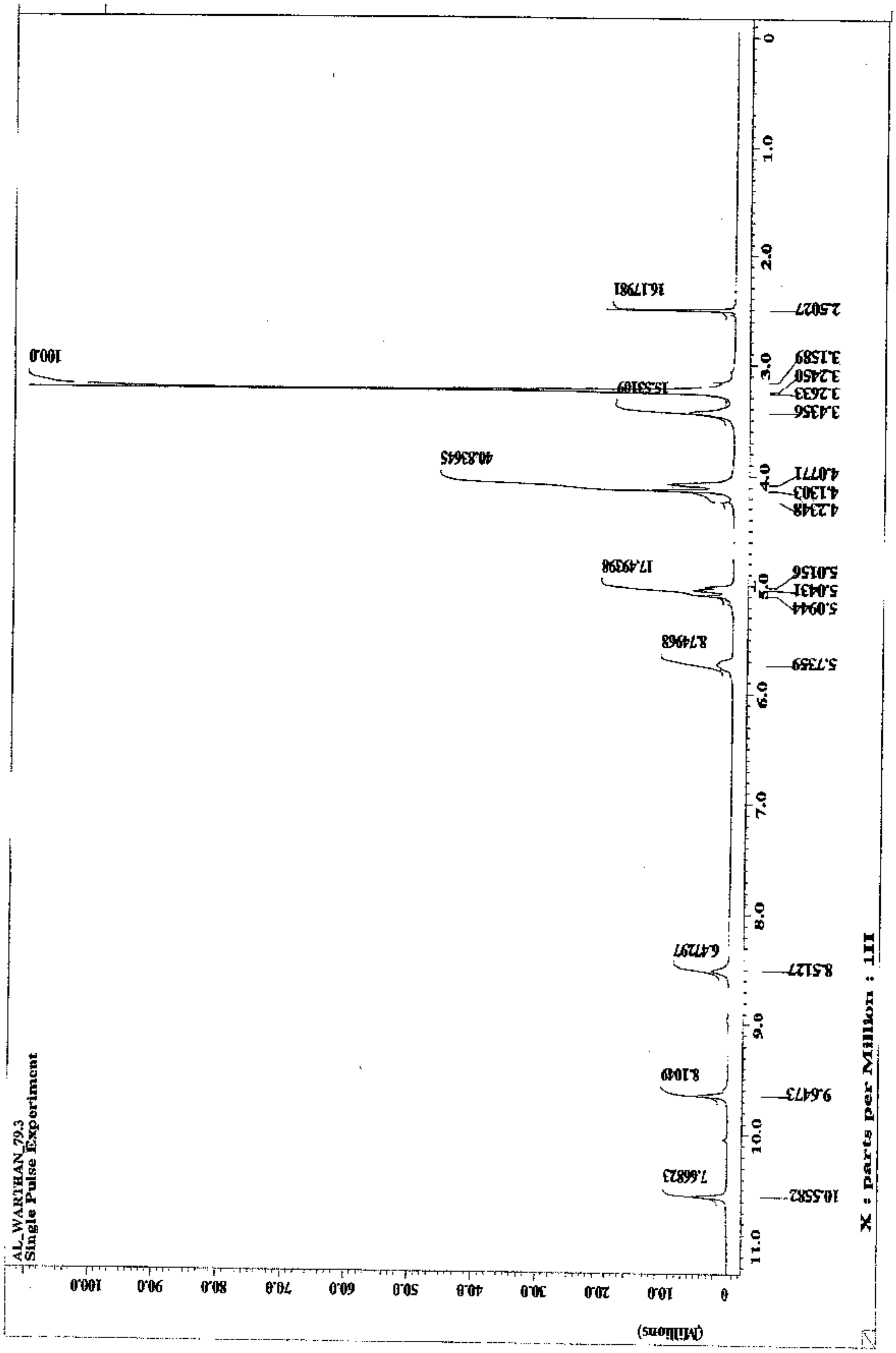
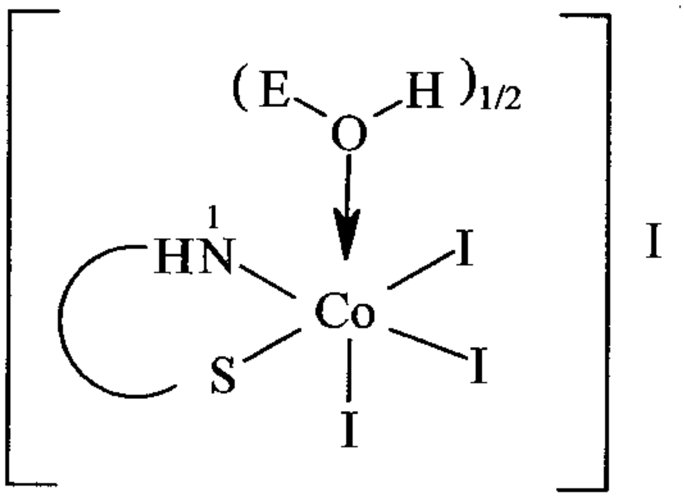


Fig. 70. ^{1}**H-NMR spectrum of [Co($C_9H_{19}N_4OS$) I_3. ½EtOH] I in d_6-DMSO.**

All these foundations suggest structure 34 for the Co(III) complex.



(structure 34)

The diamagnetic nature of this complex suggests a low-spin Co(III) configuration ($t_{2g}^{6}e_{g}^{0}$)[56,57]. The value of molar conductance (24.7 $\Omega^{-1}.cm^{2}.mol^{-1}$) in DMF suggests the electrolytic nature of this complex [41].

The IR spectrum of the blue Co(II) complex, $[Co_2(C_9H_{19}N_4OS)I_4]I$. EtOH, in Nujol mull (Fig. 71) shows that the ligand (ATHTC) coordinates in a tetradentate manner toward two Co(II) ions forming five-member ring around each Co(II) ion. The spectrum (Fig.71) shows the obscure of both the carbonyl oxygen and the thioketo groups together with the appearance of new two bands at 3558 and 2550 cm^{-1} assigned to υ(OH) and υ(SH) vibrations, respectively. The appearance of those two bands together with the appearance of two new bands at 1640 and 1531cm^{-1}, assigned to υC=N (OH) and υC=N (SH) vibrations, confirms the formation of the enol and thioenol groups. Also, the obscure of NH(1) (3210 cm^{-1}), NH(2) 3164 cm^{-1} bands while the NH(4) (3058 cm^{-1}) remains existing, indicates that the enolization and thioenolization processes are occurred *via* NH(1) and NH(2) groups. Moreover, the observation of a new band at 775 cm^{-1} assigned to υ(C-S) vibration confirms the obscure of the thioketo group *via* thioenolization. The bands at 3415 and 3375 cm^{-1} are assigned to υOH (EtOH) vibration. Meanwhile, the bands at 495, 320 287, 250 and 217 cm^{-1} are assigned to υ(Co-O)[42], υ(Co-N)[43] (enol), (Co-N), υ(Co-S)[57] and υ(Co-I)[47] vibrations, respectively.

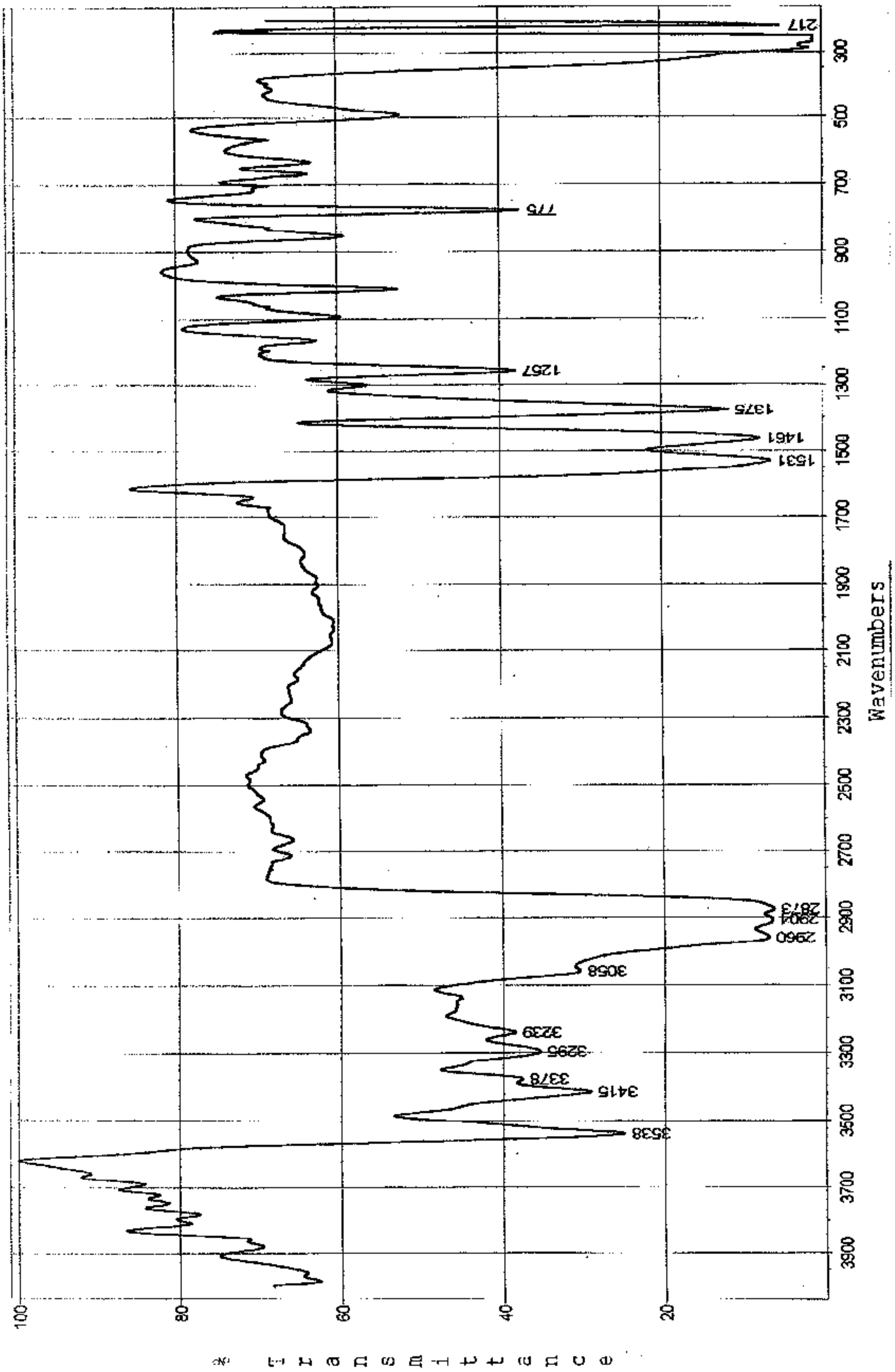
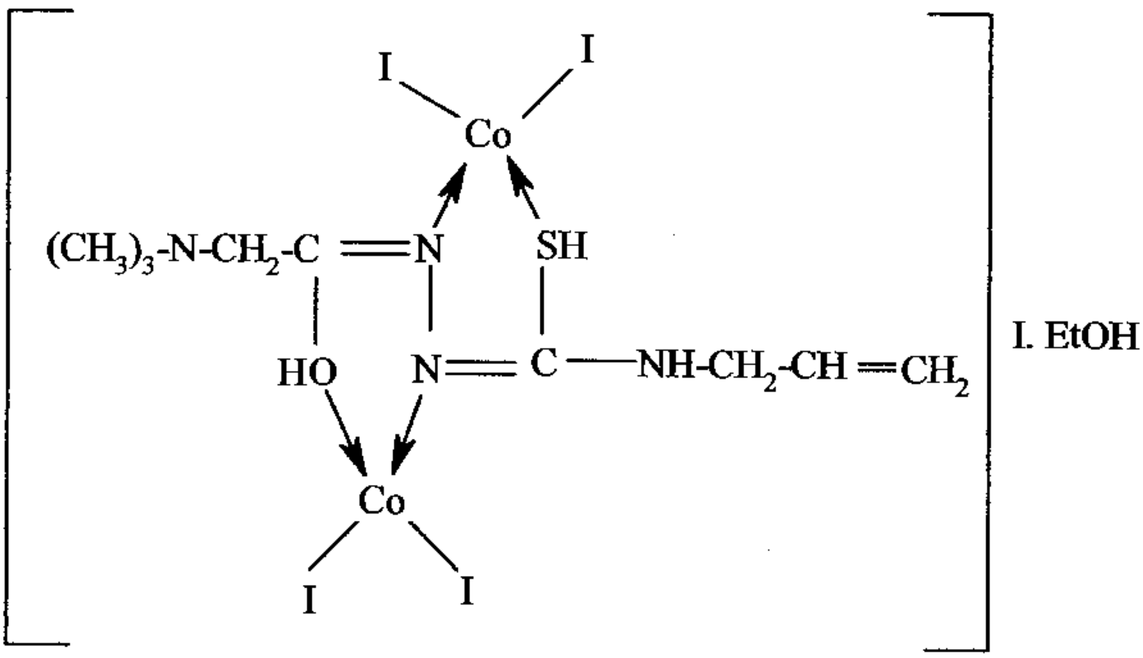


Fig. 71. Infrared spectrum of $[Co_2(C_9H_{19}N_4OS)\ L_4]\ I.\ EtOH$ in KBr.

The value of magnetic moment (4.4 B.M) is taken as evidence for the tetrahedral geometry around the two Co(II) ions. Also, the value of molar conductance in DMF (35.5 $\Omega^{-1}.cm^2.mol^{-1}$) suggest a 1:1 electrolyte[(41)].

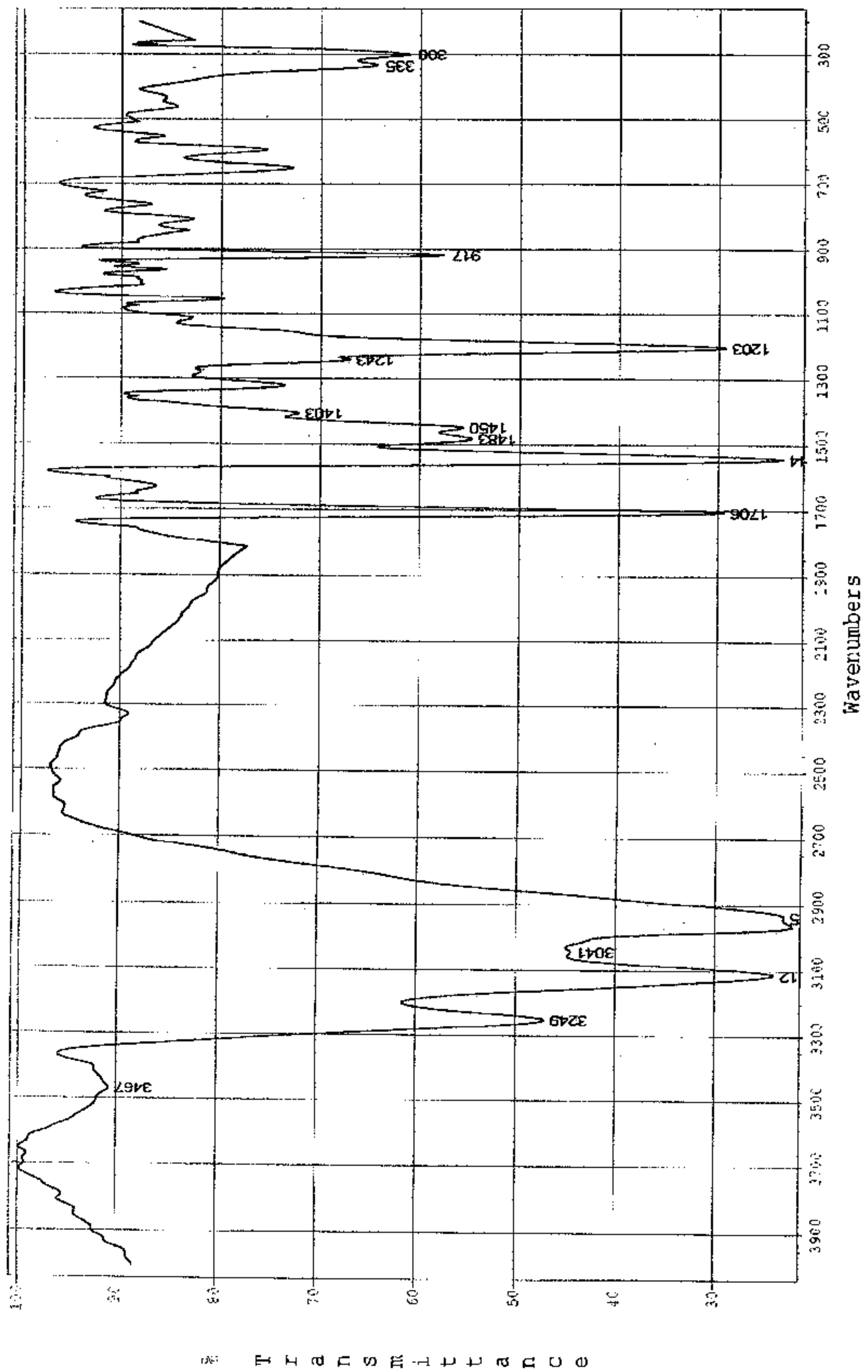
All these foundations suggest structure 35 for the Co(II) complex.



(structure 35)

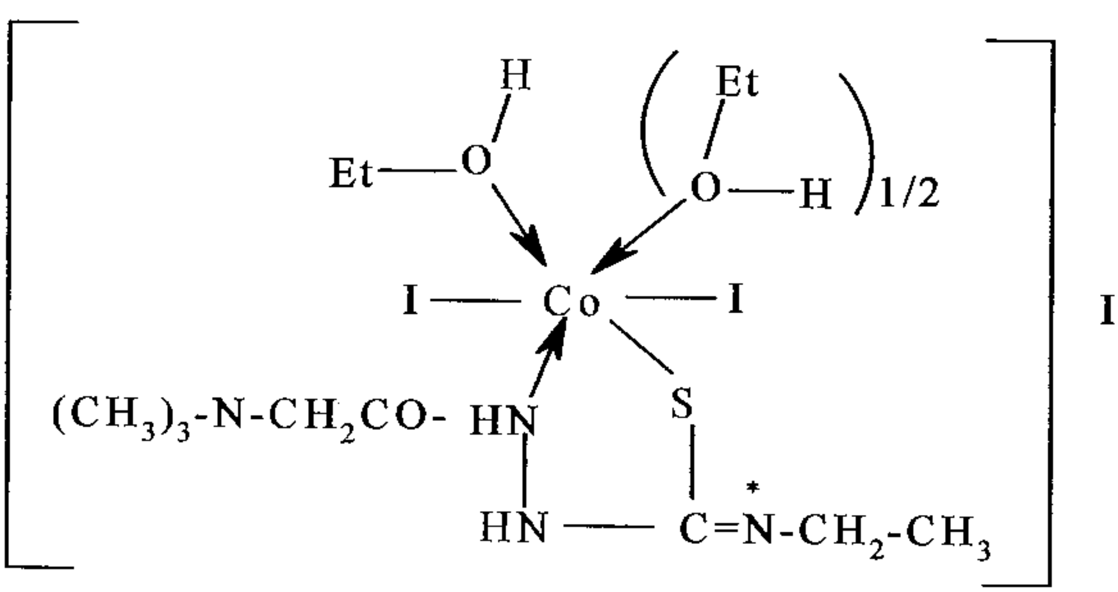
5.5. Spectral, Conductance and Magnetic Moments for the Complexes Derived from ETHTC.

The IR spectrum of the Co(III) complex in KBr (Fig. 72), $[Co(C_8H_{18}N_4OS.3/2EtOH]I$, shows that the ligand (ETHTC) behaves in a bidentate manner *via* the N(2) and the deprotonated thioenol groups. The spectrum shows the carbonyl oxygen band at 1706 cm^{-1} indicating that this group is not taking part in coordination. On the other hand, the obscure of the thioketo group at 1290 and 740 cm^{-1} in the spectrum of the free ligand (Fig. 17) together with the appearance of a new band at 760 cm^{-1} assigned to υ(C-S) vibration suggests that the thioketo group (CS) changes to the thioenol group (SH) *via* the hydrogen of the NH(2) followed by deprotonation forming five-member ring around the Co(III) ion. The band observed at 3467 cm^{-1} is assigned to υ OH (EtOH) vibration. The observation of the NH(1) and NH(2) bands at 3249 and 3112 cm^{-1} together with the obscure of the NH(4) at 3090 cm^{-1} suggests that the formation of SH is carried out *via* the NH(4) band. The observation of a new band at 1650 cm^{-1} which is obscured in the spectrum of the free ligand, is assigned to the $C=\overset{*}{N}$ group (structure, 35). The new bands



300
335
917
1203
1243
1403
1450
1483
1706
3041
3249
3467
Wavenumbers
% Transmittance

The diamagnetic nature of the Co(III) complex suggests the existence of low-spin configuration ($t_2^6e_g^o$). The value of molar conductance in DMF (31.6 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a 1:1 electrolyte[(41)]. The ^{1}H-NMR spectrum of the Co(III) complex in d_6-DMSO (Fig. 73) show three signals in the 1.0 - 4.0 p.p.m. region. The former triplet signal at 1.05 p.p.m. is assigned to the protons of $CH_3(-CH_2CH_3)$ while the triplet signal at 3.44 p.p.m. is assigned to the protons of $CH_2(CH_2CH_3)$ group. The singlet signal at 4.18 p.p.m. is assigned to the protons of the $CH_2(-CH_2CO)$ group. The three signals at 2.5, 3.55 and 10.48 p.p.m. are assigned to the protons of CH_3, CH_2 and OH group of coordinated EtOH. Finally, the two signals at 9.28 and 9.20 p.p.m. are assigned to the protons of NH(1) and NH(2) groups, respectively. The obscure of the proton of NH(4) is taken as additional evidence for the deprotonation *via* NH(4) group. All these foundations suggest structure 36 for the Co(III) complex.



(structure 36)

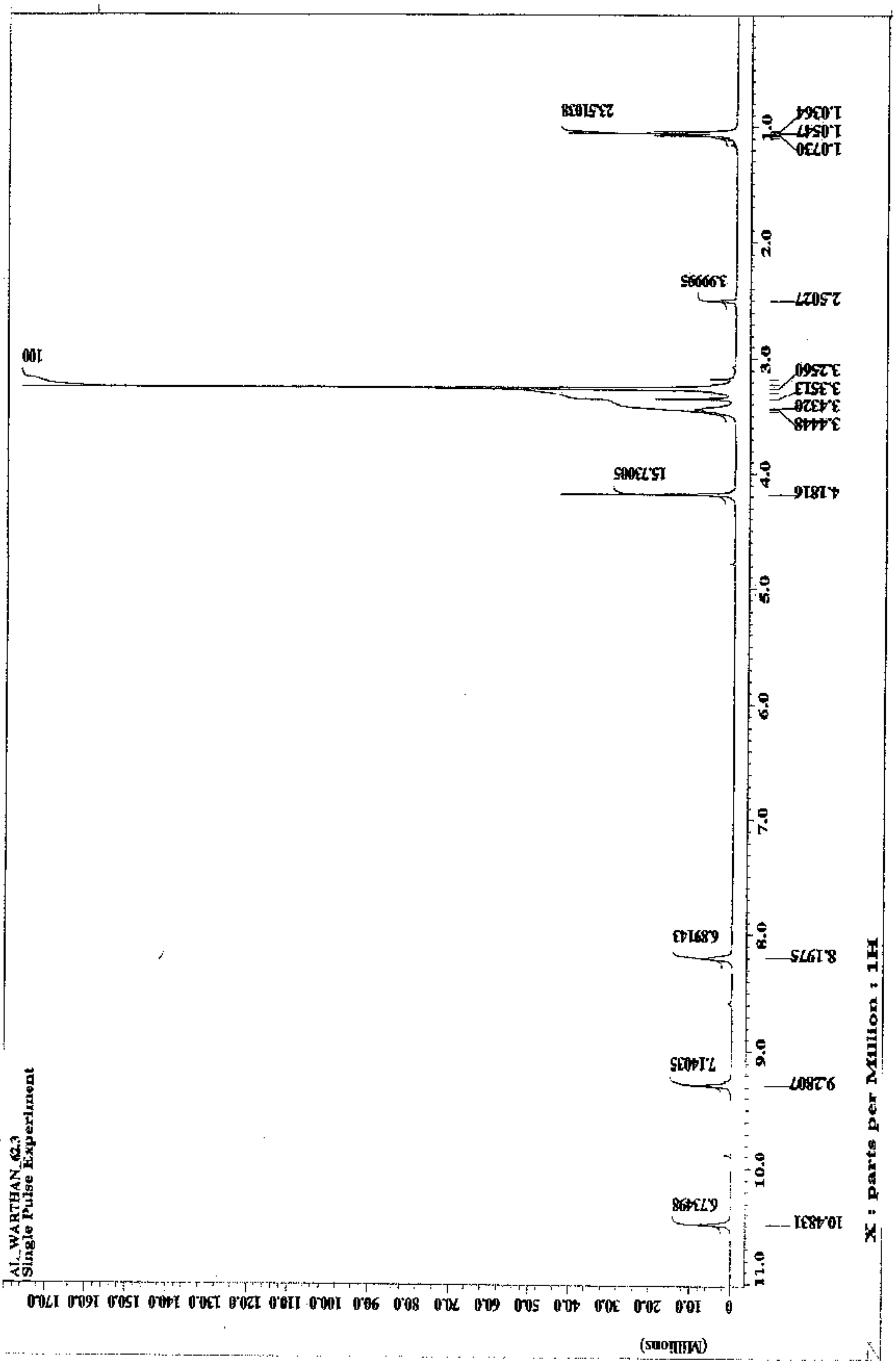


Fig. 73. ^{1}H-NMR spectrum of [Co (C_8 $H_{18}N_4OS$) I_2. 1/2 EtOH] I in d_6-DMSO.

The IR spectrum of the diamagnetic Cu(I) complex in KBr, $[Cu_2(C_8H_{18}N_4OS)I(H_2O)_3]I.\ H_2O$, (Fig.74) shows that the ligand (ETHTC) coordinates in at tetradentate manner toward two Cu(I) ions. The first Cu(I) ion coordinates *via* the carbonyl oxygen and NH(2) groups while the second Cu(I) ion coordinates *via* NH(1) and SH with deprotonation from the latter group. The IR spectrum shows four bands at 3500, 3432, 3235 and 3151 cm^{-1} assigned to υOH (hydrated), NH(1) and NH(2) groups, respectively. The disappearance of the NH(4) group suggests that this group participates in the thioenolization process forming SH group. The positive shift of the carbonyl oxygen band (1718 cm^{-1}) may suggest that this group is taken part in coordination. The absence of the two bands at 1290 and 740 cm^{-1} may suggest that this group is taken part in coordination. The absence of the two bands at 1290 and 740 cm^{-1} together with the appearance of a new band at 680 cm^{-1} assigned to υ(Cu-S) vibration. The obscure of NH(4) is followed by the appearance of a new band at 1630 cm^{-1} assigned to $\upsilon(C=\overset{*}{N})$ vibration. The bands observed at 511, 480, 350, 330 and 271 cm^{-1} are assigned to υ(Cu-O) (H_2O) , υ(Cu-O), υ(Cu-N)(NH^1), υ(Cu-N)(NH^2) and υ(Cu-S), vibrations, respectively .

The value of molar conductance (26.4 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a 1:1 electrolyte[41].

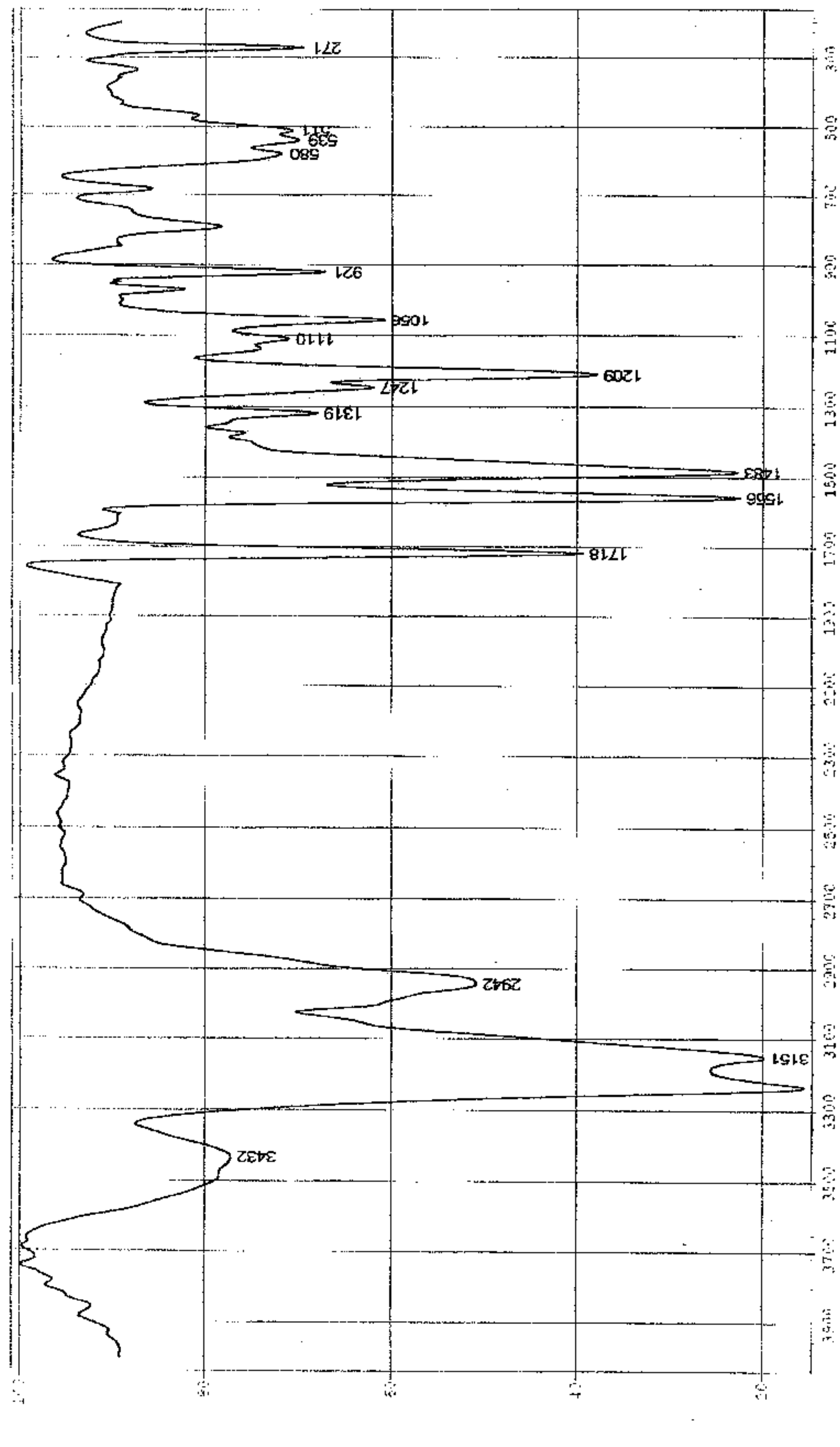
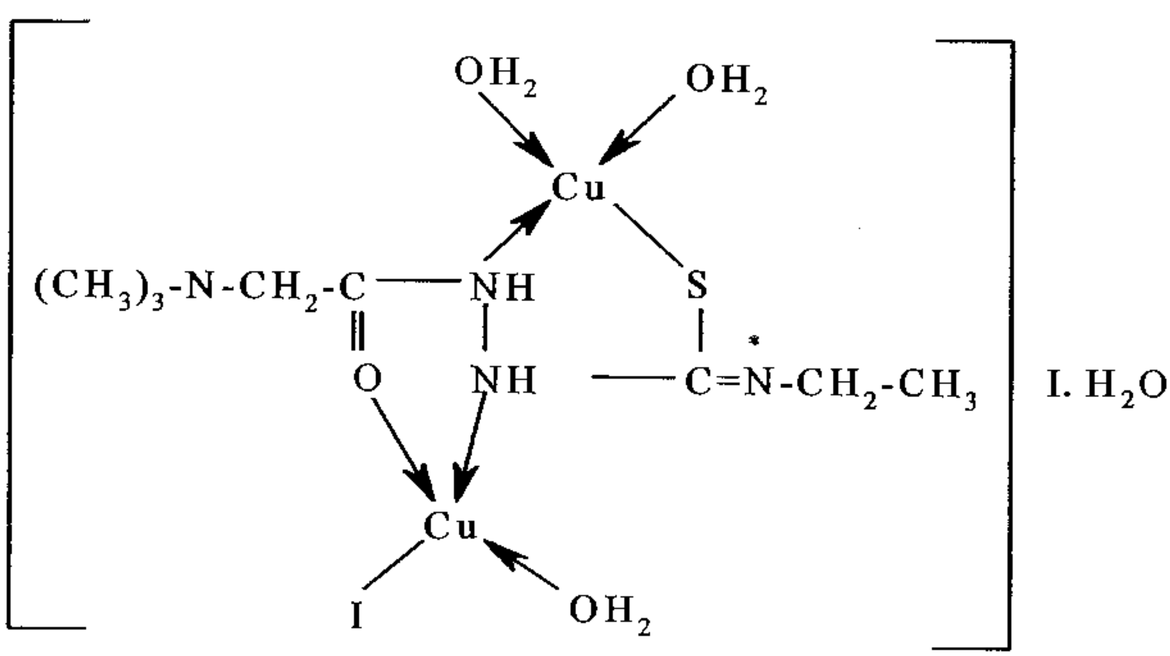


Fig. 74. Infrared spectrum of [$Cu_2(C_8H_{18}N_4OS)$ I $(H_2O)_3$] I.H_2O in KBr.

The ^{1}H-NMR spectrum of the Cu(I) complexes in d_6-DMSO (Fig. 75) $[Cu_2(C_8H_{18}N_4OS)I(H_2O)_3]I.H_2O$, shows three signals at 1.09, 3.23 and 4-10 p.p.m., downfield with respect to TMS, assigned to the protons of the $CH_3(C_2H_5$-), $CH_2(C_2H_5$-) and CH_2(-CH_2CO-) groups, respectively. The signal at 4.25 p.p.m. is assigned to the proton of H_2O. The signals at 9.45 and 8.29 p.p.m. are assigned to the protons of NH(1) and NH(2), respectively. All these foundations suggest structure 37 for this complex.



(structure 37)

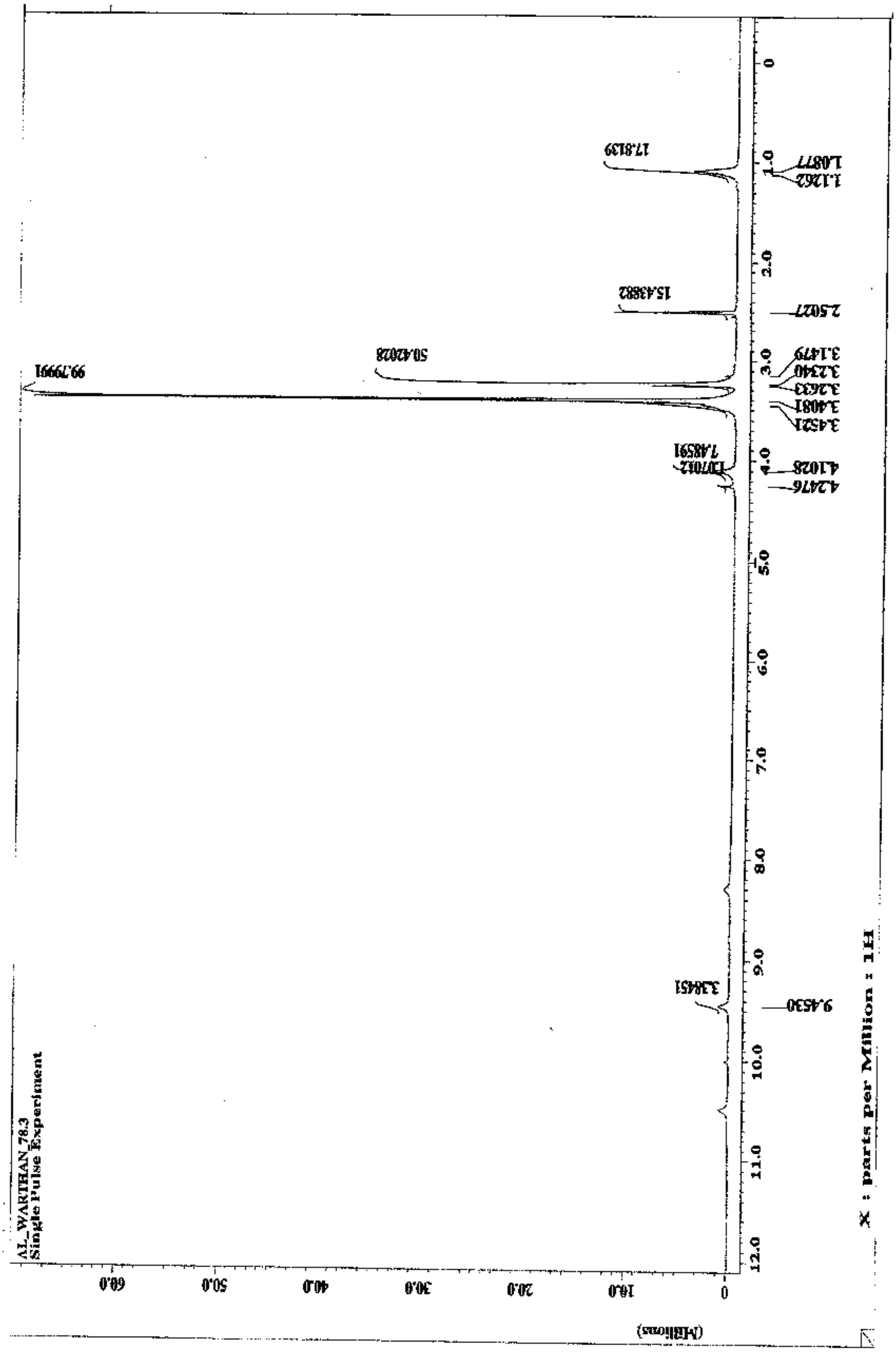
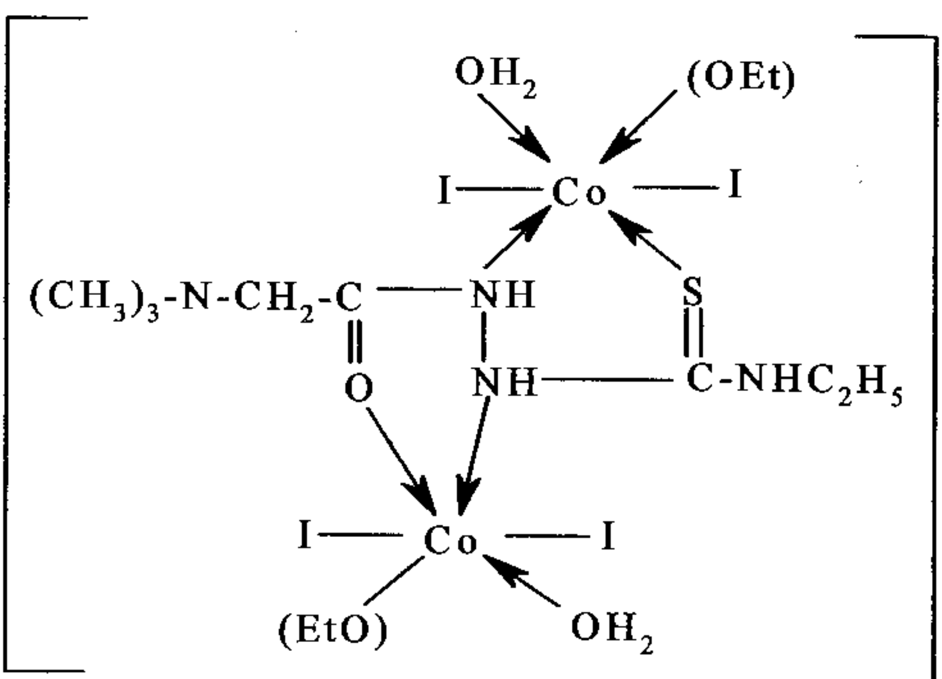


Fig. 75. ^{1}H-NMR spectrum of $[Cu_2(C_8H_{18}N_4OS)\ I\ (H_2O)_3]\ I.H_2O$ in d_6-DMSO.

The IR spectrum of the Co(III) complex, $[Co_2(C_8H_{18}N_4OS)I_4.(OEt)_2(H_2O)_2]$ I.1/2EtOH, in KBr (Fig.76) shows five bands at 3475, 3457, 3255, 3110 and 3031 cm^{-1} are assigned to υOH(H_2O), υOH (EtOH), υNH(1), υNH(2) and υNH(4) vibrations, respectively. The observation of the latter three bands at lower wavenumbers, in comparison to the IR spectrum of the free ligand (Fig.17), suggests that these groups participate in bonding as NH(1) and NH(2) groups, or influenced by coordination as NH(4) group. Also, the spectrum shows that the other bands (CO, CS) are shifted to higher or lower wavenumbers. Moreover, the bands at 505, 480, 465, 339, 325 and 287 cm^{-1} are assigned to υ(Co-O)(OEt), υ(Co-O)(OH_2), υ(Co-O)(CO), υ(Co-N)(NH^1), υ(Co-S)(CS) and υ(Co-N)(NH^2), respectively.



I. 1/2 EtOH

(structure 38)

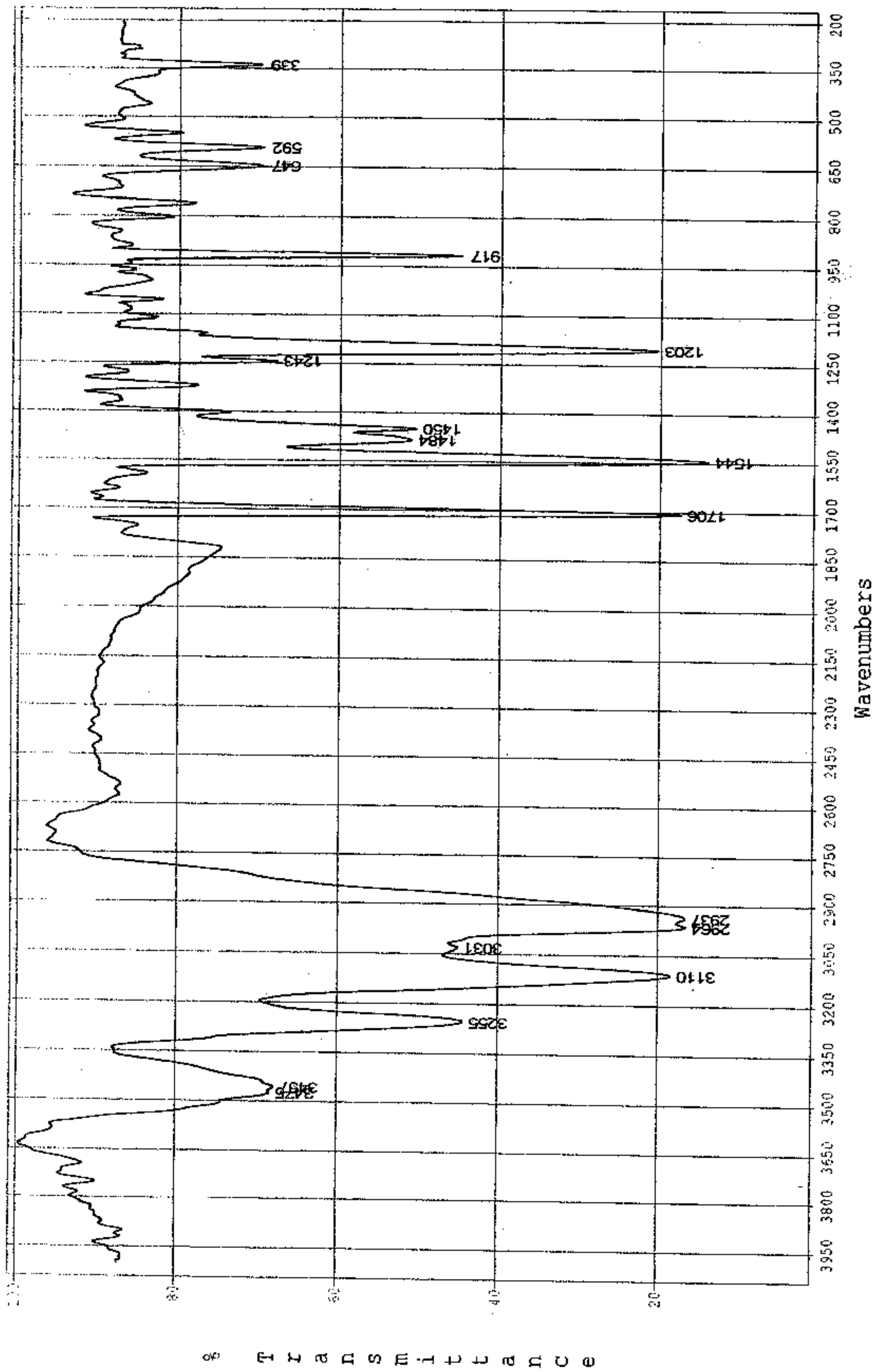


Fig. 76. Infrared spectrum of [$Co_2(C_8H_{18}N_4OS)$ L, $(OEt)_2$ $(H_2O)_2$] L, ½ EtOH in d_6-DMSO.

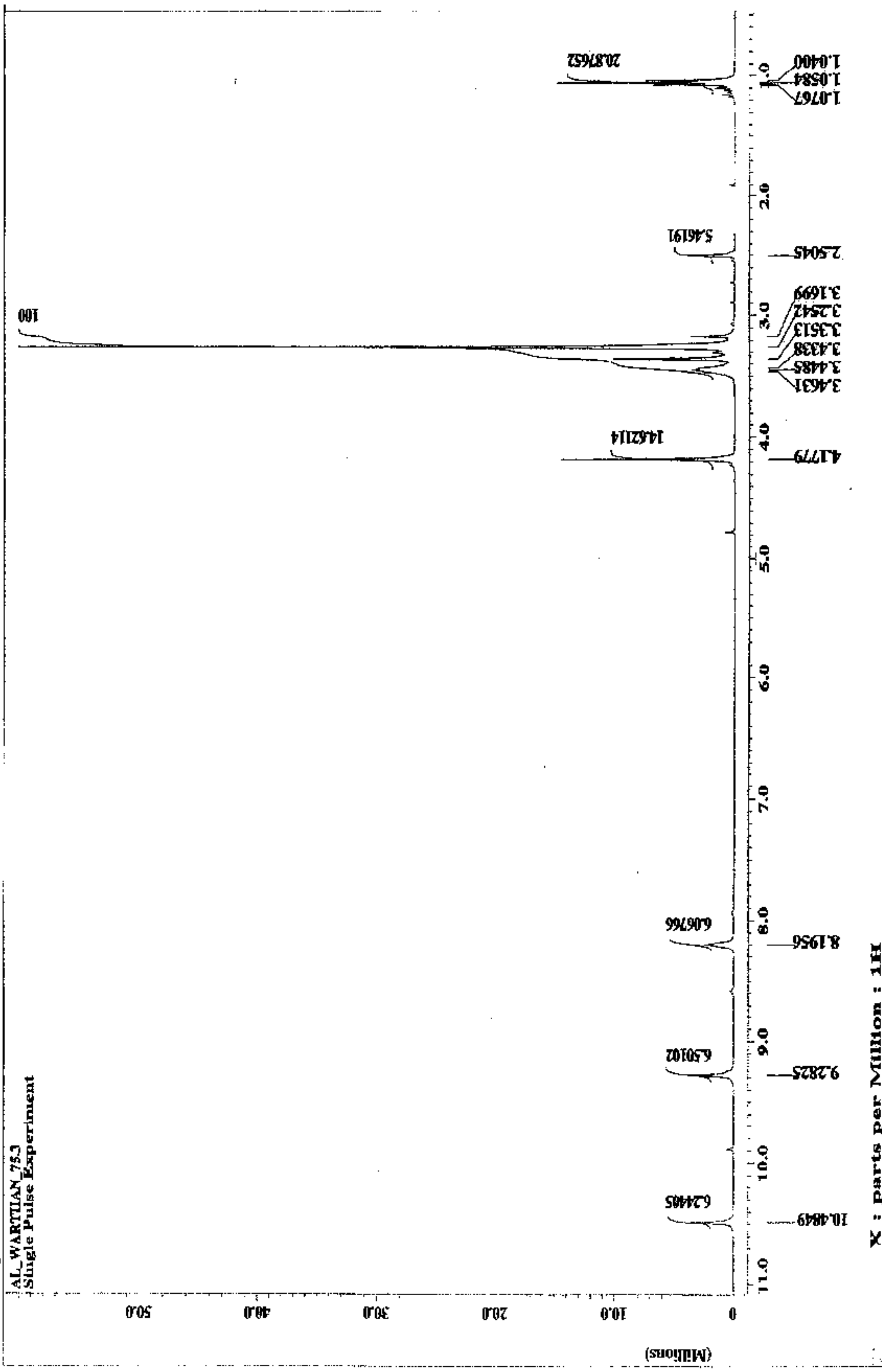
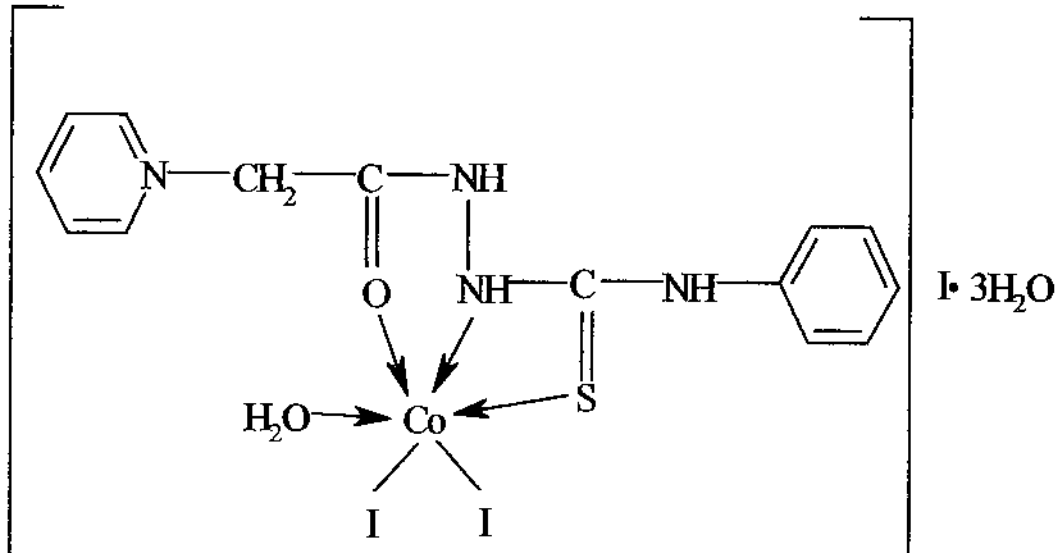


Fig. 77. ^{1}H-NMR spectrum of $[Co_2(C_8H_{18}N_4OS)\ L_4.\ (OEt)_2\ (H_2O)_2]$ L. ½ EtOH in d_6-DMSO.

The value of molar conductance in DMF (30.1 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a 1:1 electrolyte[(41)]. The ^{1}H-NMR spectrum of the Co(III) complex in d_6-DMSO (Fig.77) shows three singlet signals with equal intensities (1:1:1) at 10.5, 9.3 and 8.2 p.p.m., downfield with respect to TMS, are assigned to protons of NH(1), NH(2) and NH(4), respectively. The signals at 1.06, 3.45 and 4.18 p.p.m. are assigned to the protons of $CH_3(CH_3CH_2\text{-})$, $CH_2(CH_3CH_2\text{-})$ and CH_2 ($\text{-}CH_2\text{-}CO\text{-}$), respectively. The signals at 3.17, 3.35 and 4.25 p.p.m. are assigned to the protons of CH_3, CH_2 and OH of EtOH. All these foundations suggests structure 38 for the Co(III) complex.

5.6. Spectral, Conductance and Magnetic Moments for the Complexes Derived from PTHPC.

The IR spectrum of the Co(II) complex, $[Co(C_{14}H_{15}N_4OS)I_2.H_2O]I.3H_2O$. in KBr (Fig. 78) shows that the ligand (PTHPC) acts in a tridentate manner coordinating *via* the carbonyl oxygen, thioketo (CS) and NH(2) groups.



(structure 39)

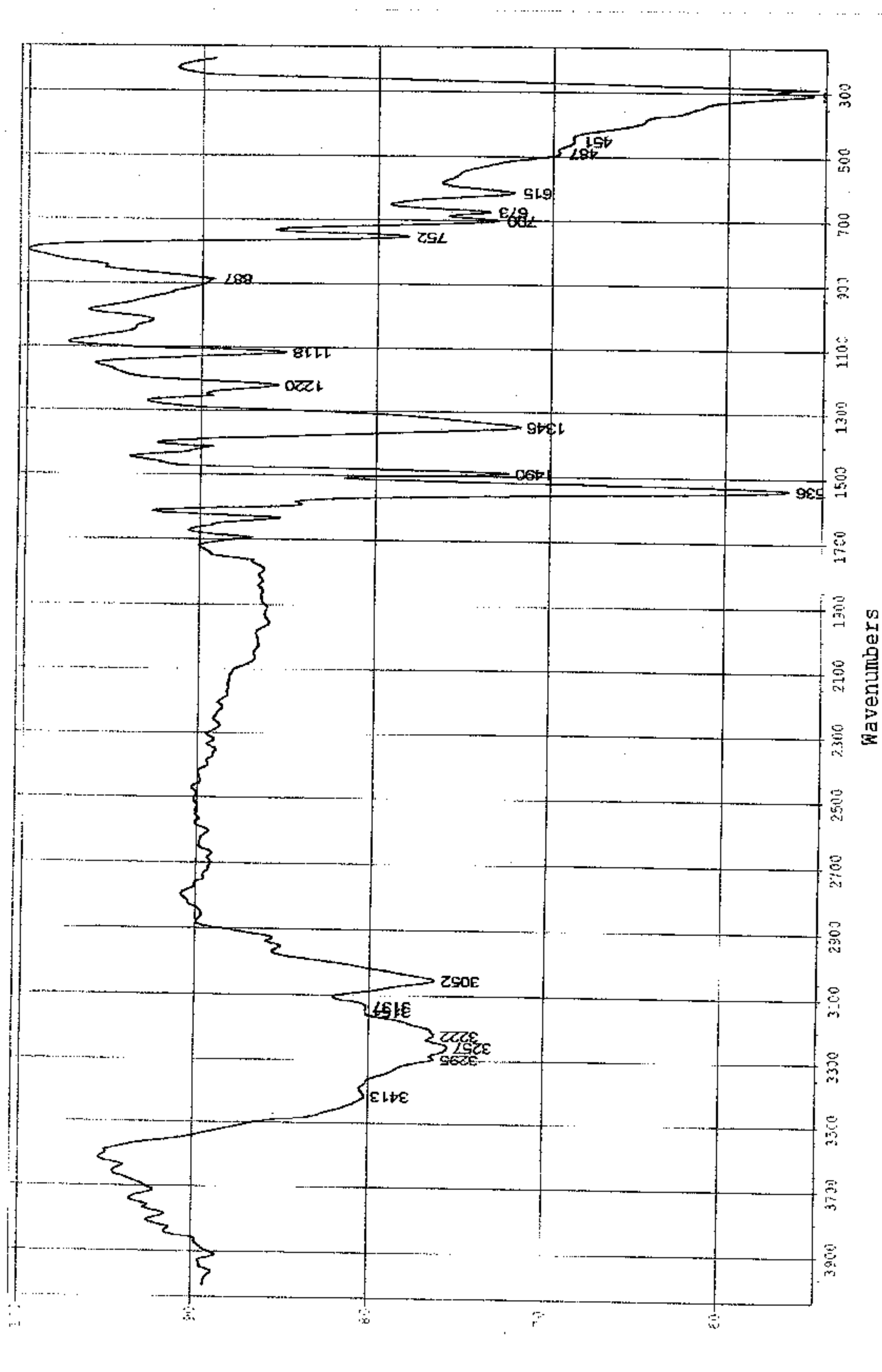
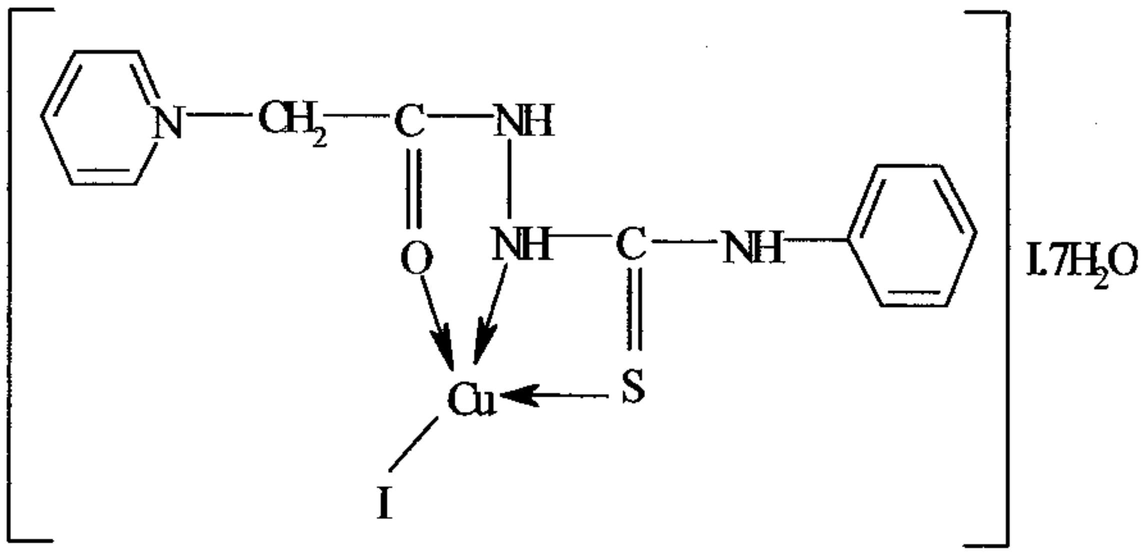


Fig. 78. Infrared spectrum of [Co($C_{13}H_{15}N_4OS$) I_2. H_2O] I.3H_2O in KBr.

All these groups suffer from negative shifts to lower wavenumbers. The bands observed at 451, 306 287 cm^{-1} are assigned to υ(Co-O)[42], υ(Co-N)[42] and υ(Co-S)[43] vibrations, respectively. The value of magnetic moment (3.6 B.M.) suggests an octahedral-geometry around the Co(II) ion. Also, the value of molar conductance in DMF (38.6 $\Omega^{-1}.cm^{2}.mol^{-1}$) suggests a 1:1 electrolytic nature[41]. All these foundations suggest structure 39. Finally, the IR spectrum of the Cu(I) complex, $[Cu(C_{14}H_{15}N_4OS)I]L\ 7H_2O$, in KBr (Fig. 79) suggests also that the ligand (PTHPC) coordinates in a tridentate manner *via* the carbonyl oxygen, thioketo and NH(2) groups. The spectrum of the Cu(I) complex is quite similar to the spectrum of the Co(II) complex (Fig.78). The ^{1}H-NMR spectrum of the Cu(I) complex in d_6-DMSO (Fig. 80) shows three singlet signals with equal intensity (1:1:1) at 10.84, 9.97 and 9.78 p.p.m., downfield with respect to TMS, assigned to the protons of NH(1), NH(2) and NH(4) groups, respectively. The multiple signals in the 7.01-8.99 p.p.m. region are assigned to the protons of the pyridyl and phenyl groups. The signal at 5.58 p.p.m. is assigned to the protons of $CH_2(-CH_2CO-)$ group. The molar conductance of the diamagnetic Cu(I) complex in DMF (29.7 $\Omega^{-1}.cm^{2}.mol^{-1}$) indicating 1:1 electrolyte [41]. All these foundations suggest structure 40 for the Cu(I) complex.



(structure 40)

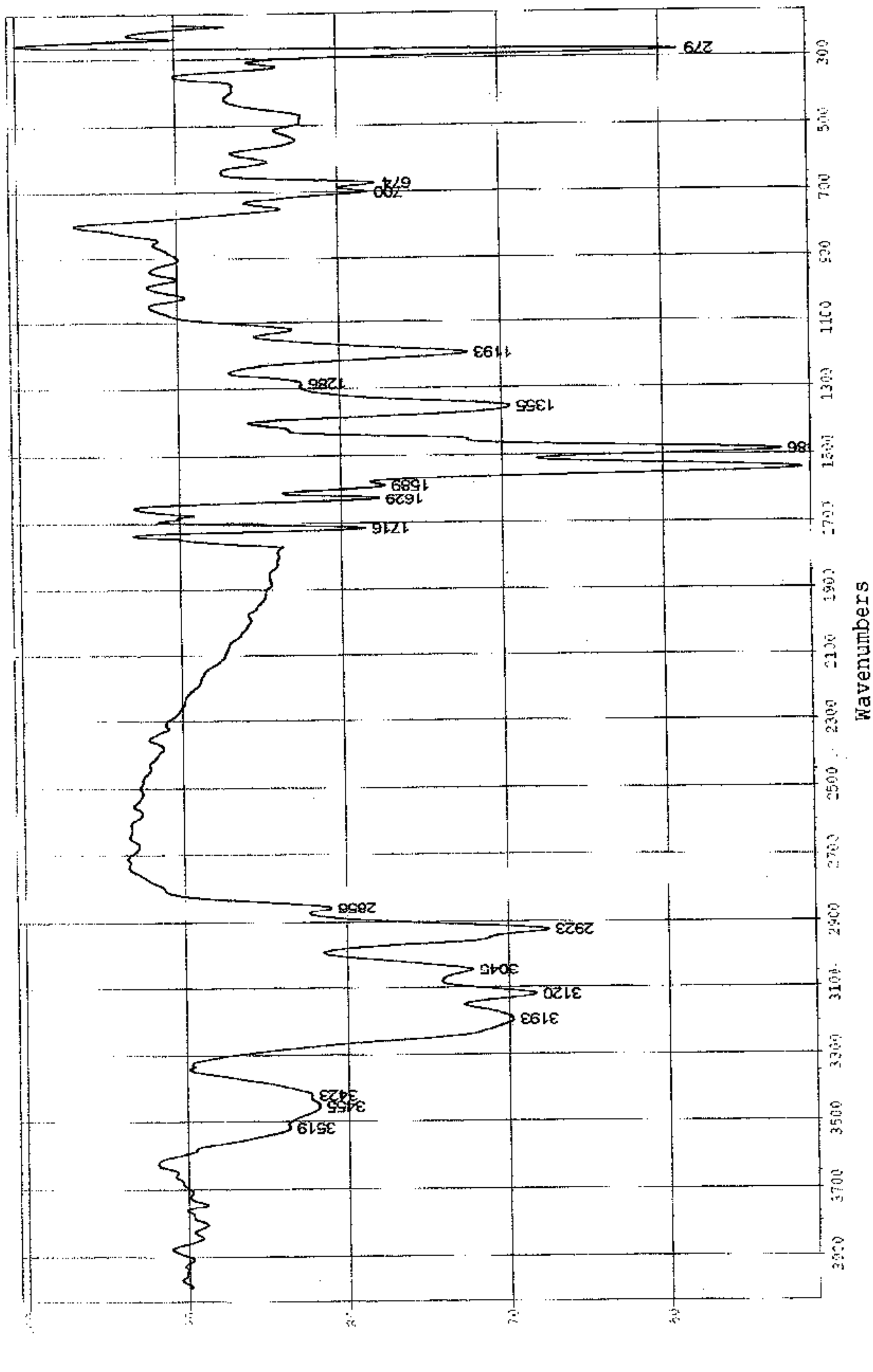


Fig. 79. Infrared spectrum of [Cu($C_{14}H_{15}N_4OS$) I] I. $7H_2O$ in KBr.

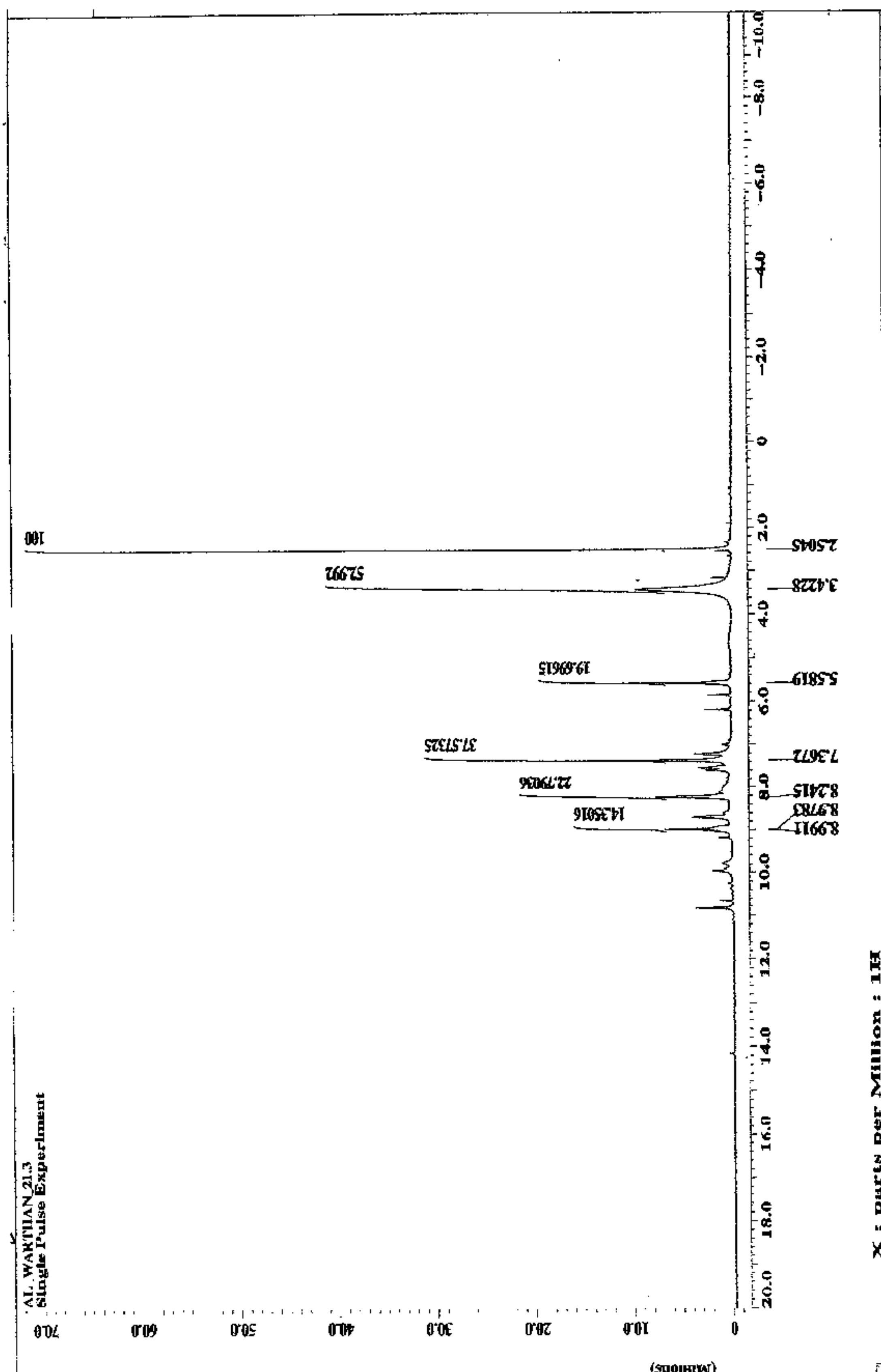


Fig. 80. ^{1}H-NMR spectrum of [Cu ($C_{14}H_{15}N_4OS$) I] I. $7H_2O$ in d_6-DMSO.

SUMMARY

The thesis comprises three main chapters :

The first chapter, *INTRODUCTION,* includes two main parts of literature survey of both tribochemistry and tribchemical reactions of hydrazides and some crown ether complexes .

First part, *Tribochemical Reactions,* includes the definition of tribochemistry, differences between tribochemistry and mechanochemistry and finally a literature survey of the most recent tribochemical reactions in the fields of organic synthesis, organometallic, inorganic and coordination chemistry.

Tribochemistry, is defined as the branch of chemistry dealing with the chemical and physicochemical changes of solids due to the influence of mechanical energy.

On the other hand, *Mechanochemistry* is defined as the branch of chemistry dealing with the chemical and physicochemical changes of substances of all states of aggregation due to the influence of mechanical energy.

The importance of tribochemical reactions is due to its wide applications in technology, chemical, metallurgical and building industries.

Second part includes a literature survey of hydrazides and some crown ether complexes. This part involves a literature survey for the recent publications carried out by us. Also, It includes the synthesis of some novel Cu(I), Cu(II) and Ru(III) complexes derived from Girard's T and formylhydrazine. Moreover, it includes the synthesis of some novel Hg(II) complexes derived from some crown ethers (DC18C6 and DB18C6). Finally this chapter is ended with the aim of work.

The **second chapter,** *EXPERIMENTAL,* contains the experimental details used in the present work. Eight ligands were used to prepare Cu(II), Cu(I), Co(II) and Co(III) complexes. These ligands are [1- (carboxymethyl) pyridinium chloride hydrazide] (G.P.), N- (3- hydoxypyridine-phenylthiourea, N'-(3-methylpyridyl)-N'-phenylthiourea, N-2-(6-methylpyridyl) -N'- thiourea, N-{[(allylamino) thioxomethyl] hydrazinocarbonyl methyl } trimethylammonium chloride, N-{[(ethylamino) thioxomethyl] hydrazinocarbonylmethyl} trimethylammonium chloride and N-{[(phenylamino) thioxomethyl] hydrazinocarbonylmethyl} pyridinium chloride.

The Cu(II) and Co(II) chloride complexes were prepared using the conventional chemical method by the reaction of the above mentioned ligands with $CuCl_2.2H_2O$ and/or $CoCl_2.6H_2O$

in ethanol. The corresponding Cu(II), Cu(I), Co(II) and Co(III) iodide complexes were prepared by tribochemical reactions using the metal chloride complexes prepared by the above method (conventional chemical method) with KI in agate mortar. The analysis of solid complexes and preparation of solutions were described. Finally, the working procedures and apparatus (conductance, IR, Uv-Vis., ^{1}H-NMR and magntic moments) were discussed.

The **third chapter**, *RESULTS AND DISCUSSION* , includes the data obtained and the proposed structures for the isolated solid complexes. The elemental analyses data of C, H, N, S, and M contents for the isolated solid complexes coincide with the contents for the proposed formulae. This chapter is subdivided into the following items:

I - Description in details the methods of preparation of the solid complexes using the conventional and tribochemical methods. Also, it involves the classification of the complexes according to the donor atoms involve in bonding. The formulae of the solid complexes were proposed on the basis of elemental analyses, spectral and magnetic data. The elemental analyses of ligands and solid complexes prepared by conventional and tribochemical reaction are shown in tables 4-6.

II- Discussion of the IR and ^{1}H-NMR spectra of the eight ligands to verify their structures and to determine the most important assignments to suggest the mode of bonding.

III- Characterization of the isolated solid complexes derived by conventional chemical method. Also, this part suggests the stereochemistry of the Cu(II) and Co(II) complexes using conductance, spectral (IR, ^{1}H-NMR) and magnetic measurements.

IV- Characterization of the isolated solid complexes derived by tribochemical reaction. Also, this part suggests the stereochemistry of the Cu(I), Cu(II), Co(II) and Co(III) complexes using conductance, spectral (IR, ^{1}H-NMR) and magnetic measurements.

All the above results suggest that these ligands react either in the keto or enol forms but most of the solid complexes are separated in the keto form. Also, the results indicate that the tribochemical reaction is accompanied by the substitution of chloride by iodide ions. Moreover, the preparation of solid complexes by tribochemical reaction is accompanied in some cases by oxidation of Co(II) to Co(III) but most of copper complexes are accompanied by reduction of Cu(II) to Cu(I). Finally, the data suggest that the stereochemistry, of most of Cu(II) complexes, have distorted-octahedral structures and few

have tetrahedral configuration around the Cu(II) ion. On the other hand the stereochemistry of all Cu(I) complexes have square-planar structure. The results suggest that most of Co(II) have high-spin octahedral structures while few of Co(II) complexes have tetrahedral structures. Finally the results of Co(III) complexes suggest that all these complexes have low-spin octahedral structures.

The thesis includes a list of 60 references and the data are represented by 80 figures, 40 structures.

REFERENCES

1- W. Ostwald, Handbuch d. Allg. Chemie, **1**, 70 (1919).

2- M. Carey-Lea, Phil. Mag., **34**, 46 (1892); **37**, 31, 470 (1894).

3- L. H. Parker, J. Chem. Soc., **105**, 1504 (1914); **113** ,396 (1918).

4- G. Tamman, Z. Elektrochem., **35**, 21 (1921).

5- M. Fink, Trans. Am. Soc. of Steel Treating, **18**, 102 (1930).

6- F. P. U. Bowden and D. Tabor, " The Friction and Lubrication of Solids" Oxford, 1958.

7- M. Fink and U. Hofmann, Z. Anorg. Allg. Chem., **210**, 100 (1933).

8- K. Peters, " Europaisches Symposium Zerkleinern", Frankfurt, 78 (1963).

9- G. Heinicke, Schmierungstechnik, **1**, 65 (1970).

10- G. Heinicke, Silikattechnik, **22**, 18 (1971).

11- G. Heinicke, " ABC Naturwissenschaften U. Technik," II, 652, Leipzig (1969).

12- G. Heinicke, Silikattechnik, **22**, 126 (1971).

13- G. Heinicke, Technik, **32**, 628, 688 (1977).

14- G. Heinicke, Chem. Prum., **25**, 508 (1975).

15- XL. Li, Y. M. Wang, D. M. Du, Z. Wen, G. X. Xiong and J. B. Meng., Science in China, Series B, Life Sciences and Earth Sciences, **40** (3), 270 (1977).

16- N. S Khrucheva, N. M. Loim, V. I. Sokolov and V. D Mafkhaev, J. Chem. Soc., Perkin Trans., **1** (16), 2425 (1997).

17- J.C. Lu, J. S. Chen, Q. D. Su and K. L. Yon, J. Chinese Universities, **18** (8), 1262 (1997).

18- H. G. Zheng, D. X .Zeng, X. Q. Xin and W. T. Wong, Polyhedron, **16** (20), 3499 (1997).

19- A. A. Doyle, S. Persons, G. A. Solan and R. E. Winpenny, J. Chem. Soc., Dalton Trans., **12**, 2131 (1997).

20- J. P. Lang and K. Tatsumi, Inorg. Chem., **37**, 24, (1998).

21- M. M. Mostata, E. A. H. Gomma, M. A. Mostafa and F. I. El-Dossouki, Spectrochim. Acta, **A**, 55 (1999).

22- M. M. Mostafa, E.A.H. Gomma, M. A. Mostafa and F. I. El-Dossouki, Synth. React. Inorg. Met-Org. Chem., **30** (1), 157 (2000).

23- M. M. Mostafa and M. H. Abdel-Rhman, Spectrochim. Acta, **A**, 2341 (2000).

24- M. M. Mostafa, R. M. El-Shazly, T. H. Rakha and M. H. Abdel-Rhman, Trans. Met. Chem., **27** (3), 337 (2002).

25- M. M. Mostafa and M. H. Abdel-Rhman, Intern. J. Chem., **14** (1), 17 (2004).

26- M. A. Hafez, A. M. Abdallah and T. H. A. Wahdan, Analyst, **116**, 663 (1991).

27- M. A. Hafez, Anal. Lett., **225** (9), 1779 (1992).

28- A. I. Vogel, " Quantitative Inorganic Analysis", Longmans, London (1961).

29- M. Masui and H. Ohmori, J. Chem. Soc., **A**, 153 (1969).

30- A. Braibanti, F. Dellvalla, M. A. Pellinghelli and E. Leporati, Inorg. Chem., **7**, 1430 (1968).

31- K. Nakanishi, " Infrared Absorption Spectrossopy", 2nd. Edit., Holden. Day, Inc., USA (1977).

32- M. M. Mostafa, A. M. shallaby and A. A. El-Asmy, Trans. Met. Chem., **6**, 303 (1981).

33- C. N. Rao and R.Venkataraghave, Spectrochim. Acta, **7**, 140 (968).

34- M. Mashima, Bull.Chem. Soc., Japan, **37**, 974 (1964).

35- J. I. Bullock and H. A. Tajmir-Riahi, J.Chem. Soc. Dalton Trans., 34 (1978).

36- R. M. Silverstein, G. C. Bassler and T. C. Morrill, " "Spectrometric Identification of Organic Compounds" 5th . Edit., John Wiley, New York (1991).

37- M. Hesse, H. Meier and B. Zeeh, " Spectroskopische Methoden in der Organischem Chemie", Georg Thieme Verlag, Stuttgart, New York, 1987.

38- M. M. Mostafa and D. X. West, Trans. Met. Chem., **8**, 312 (1983).

39- E. M. Shoukry, H. A. Bayoumi and M. M. Mostafa, Trans. Met. Chem., **25**, 73 (2000).

40- A. A. El-Asmy and M. M. Mostafa, Polyhedron, **2** (7), 591 (1983).

41- W. J. Geary, Coord. Chem. Revs., 7, 81 (1971).

42- J. R. Ferraro, " Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971.

43- A. Brown, G. Butler and W. R. Mc Whinnie, Inorg. Chim. Acta, **25**, 121 (1997).

44- A. C. Fabretti, G. C. Franchini and G. Peyronel, Trans. Met. Chem., **3**, 363 (1978).

45- M. J. Campbell and R. Grzeskowiak, J. Chem. Soc., A 396 (1967).

46- M. Kato, H. B. Jonassen and J. C. Fanning, Chem. Rev., **64**, 99 (1964).

47- J. R. During, W. A. McAllister and E. E. Mercer, J. Inorg. Nucl. Chem., **29**, 1441 (1967).

48- B. J. Hathaway and D. E. Billing., Coord. Chem. Revs., **5**, 143 (1970).

49- F. A. Devillanova and G. Verani, J. Inorg. Nucl. Chem., **41**, 1111 (1979).

50- F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry. A Comprehensive Text, 3rd. Edit. Interscience, New York (1972).

51- A. M. Gouge and J. F Geldard, Inorg. Chem., **17**, 270 (1978).

52- A. B. P. Lever, " Inorganic Electronic Spectroscopy" 2nd. Edit., Elsevier, Amsterdam (1984).

53- L. J. Bellamy, " The Infrared Spectra of Complex Molecules, " Methuen, London, 1958.

54- Y. Nishida and S. Kida, Bull. Chem. Soc., Japan, **45**, 461 (1972).

55- J. Ferguson, J. Chem. Phys., **40**, 3406 (1964).

56- M. A. Hitchman, Inorg. Chem., **16**, 1985 (1977).

57- F. L. Urbach, R. D. Bereman, J. A. Topich, M. Hariharan and B. J. Kalbacher., J. Am. Chem. Soc., **96**, 5063 (1974).

58- F. A. Cotton and M. D. Meyers, J. Am. Chem.Soc.,**82,** 5023 (1960).

59- L. Viaene, J. D'Olieslager, A. Ceulemans and L. G. Vanquickenborne, Inorg. Chem., **18**,1405 (1979).

60- G. A. Katsoulos, G. E. Manoussakis and C. A. Tsipis, Polyhedron, **3**(6),735 (1984).